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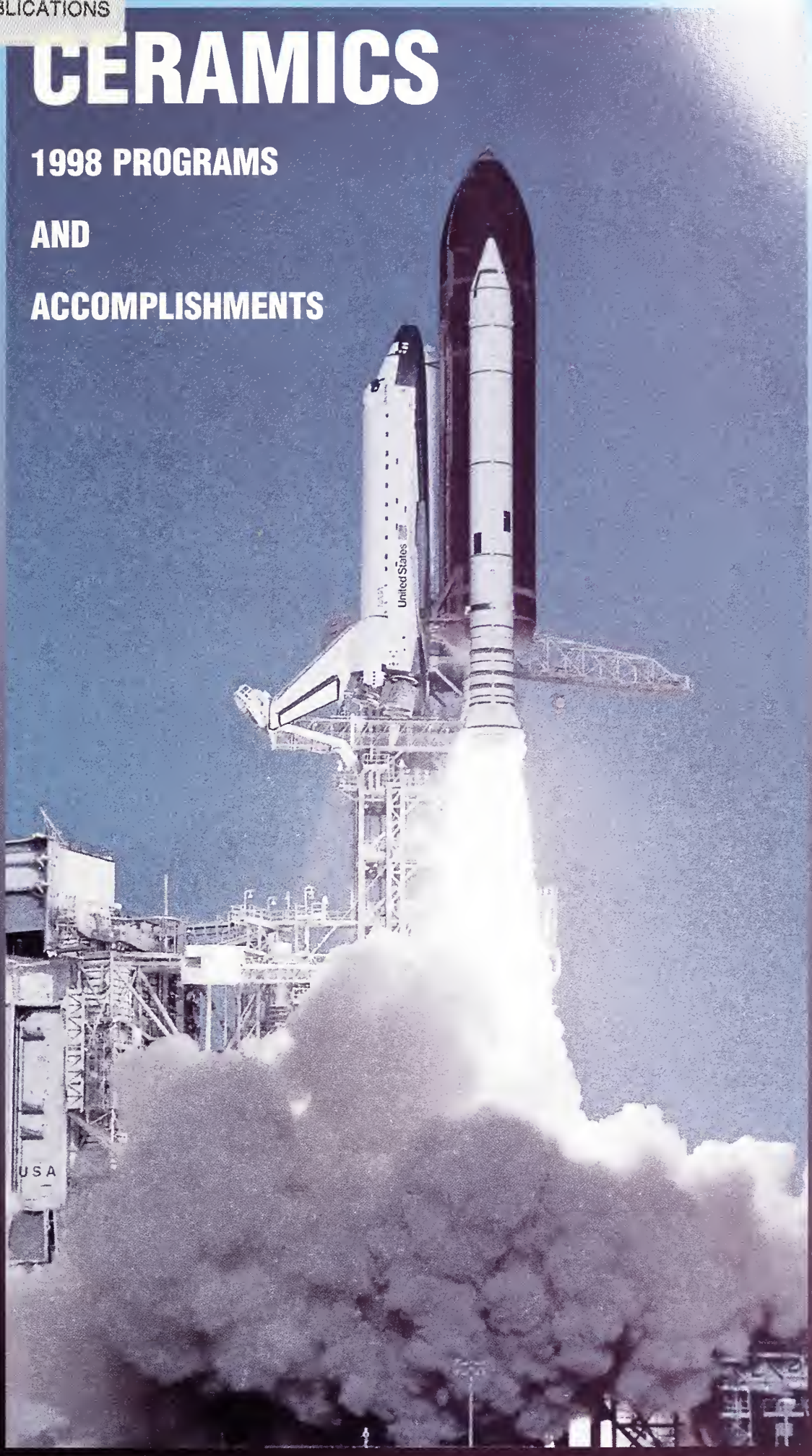
CERAMICS

1998 PROGRAMS AND ACCOMPLISHMENTS



MATERIALS SCIENCE AND ENGINEERING LABORATORY

NISTIR 6247

UNITED STATES DEPARTMENT OF COMMERCE

TECHNOLOGY ADMINISTRATION

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

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1999

Materials for a Wide Range of New Technologies

Sophisticated aerospace, biomedical, electronics and communications technologies require the use of ceramic materials which have unique properties, allowing improved performance or new capabilities. MSEL's Ceramics Division Program addresses needs in measurement, characterization and fundamental understanding required to effectively and economically utilize these materials.

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TECHNOLOGY ADMINISTRATION
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MATERIALS SCIENCE AND ENGINEERING LABORATORY

CERAMICS

1998 PROGRAMS AND ACCOMPLISHMENTS

Stephen W. Freiman, Chief

Stanley J. Dapkunas, Deputy

NISTIR 6247

January 1999

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EXECUTIVE SUMMARY

The mission of the Ceramics Division can be stated as follows:

Work with industry, standards bodies, academia, and other government agencies in providing the leadership for the Nation's measurements and standards infrastructure for ceramic materials.

The activities of the NIST Ceramics Division are organized in the form of Programs, emphasizing a desire to foster collaborations within the Division as well as throughout the Materials Science and Engineering Laboratory, and to conduct focused activities on a scale that can lead to greater benefits for the U.S. ceramics community. The Programs are made up of projects whose primary goal is the development of measurement techniques and standards. Activities such as the development of Standard Reference Materials and databases are integrated within the relevant Programs. At the same time, we continue to maintain a Division management structure in the form of Groups.

Our definition of "ceramics" has broadened to include a wide range of materials of particular interest for electronic and optoelectronic applications. While many of these materials fall in a category generally thought of as semiconductors, there are common themes such as phase content, the role of microstructure, and their brittle nature. These materials are frequently used in film form, and our newly formed Ceramic Thin Film Program is addressing generic measurement issues associated with a broad range of applications for thin film devices. During the past year we established a panel representing the electronic and optoelectronic industries to help oversee the Film Program and advise us as to the measurement and standards needs of these communities.

This year we are very pleased that the Synchrotron Radiation Team of Andrew Allen, David Black, Harold Burdette, Daniel Fischer, Gabrielle Long, Richard Spal, and Joseph Woicik, has been awarded a Bronze Medal by NIST. This team has created unique x-ray measurement facilities at both the National Synchrotron Light Source at the Brookhaven National Laboratory and at the Advanced Photon Source at the Argonne National Laboratory. They address an important aspect of our mission by making unique facilities coupled with technical expertise available to researchers from both industry and academia. The availability of such measurement capabilities has led to a number of significant accomplishments over the years.

We continue to look for improved ways to develop meaningful communication with our customers, i.e. the engineers and scientists in both companies and universities who use the measurement tools that we are developing. Workshops continue to be an important way for us to establish industrial priorities. Another technique for improved communication which we have found is through consortia where direct commentary and feedback from the members occurs frequently. As an example, the Ceramic Processing Characterization Consortium has grown to $\approx$ 78 members. This Consortium is designed to maximize the dialogue between NIST and the industrial members in order to get direct input as to their measurement needs. We are also

increasingly using the World Wide Web as a means of disseminating critical data and measurements to our customers through a vehicle that we call "The Ceramic WebBook."

Two Programs (High Temperature Superconductivity and Evaluated Materials Data) no longer appear in this report. In the case of high temperature superconductivity, all of the work now involves determination of phase diagrams and is described under the newly formed Phase Equilibria Program. The work on evaluated data is either discussed directly in the program which it impacts, e.g. Phase Equilibria, or is listed in the section entitled "Other Ceramics Division Projects." This latter section encompasses several important areas including data and x-ray SRM's which do not clearly fit under other programmatic descriptions.

Stephen W. Freiman
Chief, Ceramics Division

CERAMIC COATINGS

The Ceramic Coatings Program is a measurement and characterization effort which addresses the processing reproducibility and performance prediction of thermal-spray deposited ceramic coatings. The program addresses plasma spray deposited and physical vapor deposited ceramic thermal barrier coatings used in aircraft and land-based turbines and diesel engines and wear resistant coatings used in many applications. These materials are a significant portion of the one billion dollar thermal spray market. Collaborations have been established with industrial organizations including Pratt and Whitney, General Electric, Caterpillar, METCO, Praxair (an ATP awardee), as well as the Thermal Spray Laboratory at the State University of New York at Stony Brook, NASA Lewis Research Center and the Thermal Spray Laboratory at Sandia National Laboratory. The program includes collaboration with the National Mechanical Engineering Laboratory, in Japan, to examine functionally gradient materials. Collaborations are also underway with Bundesanstalt fur Materialfurschung und -prufung) (BAM) and Deutsche Forschungsanstalt für Luft-und Raumfahrt (DLR) , both in Germany, for the development of characterization techniques for thin, hard coatings.

Participants in the NIST program are located in the Ceramics, Materials Reliability, and NIST Center for Neutron Research of the Materials Science and Engineering Laboratory and the Chemical Science and Technology Laboratory.

The approach taken in the plasma-spray (PS) research has been to build on the analytical capabilities at NIST and the material processing capabilities of collaborators. The program has the following elements:

- development of techniques for characterization of physical and chemical properties of stabilized zirconia and tungsten carbide feedstock to provide data for increased processing reproducibility as well as data required for production of a Standard Reference Material suitable for calibration of light-scattering size distribution instruments used in industry for analysis of PS powder;

- development of scattering techniques to determine the quantity, size and orientation of porosity and microcracks in PS ceramic coatings suitable for use in modeling the thermomechanical behavior of these materials;

- development of methods to measure chemical, elastic modulus, and thermal properties on a scale suitable for use in microstructural models of behavior;

- development of techniques to model thermomechanical behavior of thermal barrier coatings to enable more reliable performance prediction;

- development of techniques for accurate measurement of the thermal conductivity of PS and PVD coatings, by use of the guarded hot plate technique suitable for incorporation in ASTM

standards and by the pulsed laser heating technique, to provide a method for comparison with routine industrial techniques; and

- development and refinement of more sensitive methods for accurate analysis of oxide phases and residual stresses which affect performance and durability of coatings.

Research on chemical mapping of powders and microstructures is conducted in the Microanalysis Division of the Chemical Science and Technology Laboratory. Thermal property research is conducted in the Materials Reliability and Metallurgy Divisions. The NIST Center for Neutron Research participates in phase analysis and residual stress measurement projects. A strong attribute of the coatings research program is the use of common materials for which complementary data can provide a more complete understanding of processing-microstructure-property relationships.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Characterization of Thermal Spray Zirconia Powders

Principal Investigators: Stanley J. Dapkunas, Patrick Pei, James F. Kelly, Judith Stalik (Center for Neutron Research) and Eric Steel (Chemical Science and Technology Laboratory)

Technical Objective:

The objective of this research is to develop measurement methods for those characteristics of thermal spray feedstock which determine the microstructure and properties of ceramic coatings.

Technical Description:

Feedstock powders are an important determinant of the final microstructure, properties, and wear resistance of coatings. Important powder characteristics include particle size distribution, chemical composition, phase content, flow, and thermal properties. This program attempts to develop a comprehensive understanding of the interrelationships among powder, deposition behavior, microstructure, and properties. This is accomplished by conducting a broad range of characterizations on a given powder or deposit.

Collaborative research is emphasized. The NIST effort focuses on powder characterization, while plasma spray deposition is conducted by others. The combined results are analyzed jointly to relate powder properties to process parameters, microstructure, and performance. Earlier research addressed the role of organic binders in zirconia feedstock on the thermal shock behavior of coatings and the role of particle size distribution on spray behavior. Subsequent research has been conducted in cooperation with a broad range of powder producers, plasma spray equipment and analytical instrument manufacturers, and coatings producers and culminated in the development of SRM 1982, yttria stabilized zirconia for thermal barrier coatings, for the calibration of particle size distribution measurement instruments. This research has been extended to the development of SRM 1984 for size distribution of tungsten carbide/cobalt feedstock, important for wear resistant coatings.

External Collaborations:

This research is conducted in cooperation with the thermal spray industry, universities and government laboratories. Technical collaboration with organizations representing engine manufacturers, material manufacturers, spray equipment and instrument suppliers includes: Pratt & Whitney, General Electric, Caterpillar, Praxair, METCO, Zircoa, TAFA, Metech, H. C. Stark, Leeds and Northrup, Horiba, Sandia National Laboratory, Osram/Sylvania, and the State University of New York at Stony Brook.

Planned Outcome:

The planned outcome of this research is the development of analytical methods which will enable manufacturers to improve process control and deposition efficiencies, and material specifications. Standard Reference Materials (SRM 1982, SRM 1984) will be produced in support of these methods.

Accomplishments:

Early research established an empirical relationship between organic binder content of spray dried and sintered yttria stabilized zirconia plasma spray feedstock and thermal shock resistance of coatings made from that powder. This work enabled tighter feedstock specifications by gas turbine manufacturers. Subsequent collaborative research culminated in the development of SRM 1982 for the calibration of particle size distribution measurement. Additional research in collaboration with the Sandia National Laboratory has utilized SRM 1982 to determine the role of size fractions on behavior in the plasma spray process.

Feedstock research has encompassed development of SANS techniques for the analysis of phase contents in zirconia powder by SANS and has been extended to analysis of zirconia deposits. This technique reduces the ambiguity associated with the presence of overlapping peaks observed with x-ray diffraction and allows measurement of phase contents critical to long-term stability of thermal barrier coatings.

SRM 1984, Tungsten Carbide/Cobalt for particle size distribution is nearing completion. Two candidate materials, fused and crushed and spray dried and sintered, have been selected and distributed to industrial and academic participants for analysis.

Publication:

S. J. Dapkunas, "Measurement Methods and Standards for Processing and Application of Thermal Barrier Coatings," Journal of Thermal Spray Technology, Vol. 6 (1), 67-76 (1997).

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Database Development for Thermal Spray Coatings

Principal Investigators: Ronald G. Munro and Stanley J. Dapkunas

Technical Objective:

The objective of this project is to provide a focused collection of evaluated data on the thermal and mechanical properties of ceramic coatings that may be useful in determining relations among properties and processing parameters.

Technical Description:

Ceramic coatings provide thermal insulation, wear resistance, and corrosion protection and allow components made from conventional materials to be used at temperatures higher than what the conventional material alone could usefully sustain. As a result, ceramic coatings extend the useful lifetime of the components and enable the application apparatus to be operated with a higher thermodynamic efficiency. Extensive applications of coatings are found in aircraft engines, stationary gas turbines, and diesel engines.

While the materials used for coatings may have the same nominal chemical composition as their counterpart bulk ceramics, the context in which the data for ceramic coatings are considered often differs from that of bulk materials because of the presence of an intermediate bond coat and a substrate and because of the dimensional and microstructural differences. Currently, there exists no publicly accessible, numeric property database relating to the special nature of ceramic coatings and their applications.

Planned Outcomes:

A database of evaluated thermal and mechanical property data relating to the characteristics and applications of ceramic coatings will be established. Data from an initial set of approximately 100 papers will be collected and evaluated during the first year of the project, and a mature database should be established within three years.

Accomplishments:

A preliminary study was conducted in FY1998 to examine the feasibility and usefulness of developing a materials property database for ceramic coatings. A sampling of the published literature, consisting of approximately 50 papers, was collected from a variety of journals. The papers were reviewed to determine what kinds of information were being reported or used and what data issues were considered to be the most important. It was found that greater attention was given to the material processing information than is commonly found in papers on bulk structural ceramics,

but the range of properties needed for applications was essentially the same for the two types of ceramic materials. The most commonly reported mechanical and thermal properties of ceramic coatings were hardness and thermal conductivity. Hardness was often used as an indicator of the quality of the deposition product (the coating), while thermal conductivity was used as an indicator of the effectiveness of the coating as a thermal barrier. It was also found that the experimental methods needed for the measurement of the properties of thin coatings often are different in important procedural aspects from those used for bulk ceramics. For example, indentations from conventional hardness measurements using a diamond indentor tend to penetrate the coating and engage the substrate, thereby invalidating the hardness measurement for the coating. Techniques using nanoindentation and instrumented indentation can be used to resolve this problem. While the nature of the test remains the same, the details of the application differ.

From this preliminary study it is clear that the information needed for ceramic coatings differs significantly in *content* from what is needed for bulk ceramics, and therefore an effort focused specifically on ceramic coatings is desirable. However, the *form* of the available information is not significantly different from that encountered with bulk ceramics. Hence, our previous work on bulk structural and superconducting ceramics can be adapted readily to the development of a database for ceramic coatings.

As a result of this study, we are initiating the development of a new database of material properties for ceramic coatings. The initial emphasis for this database will be on thermal barrier coatings, and the primary focus will be on the thermal and mechanical properties of yttria stabilized zirconia coatings, $(1\text{-}x)ZrO_2 \cdot xY_2O_3$, with the mass fraction of Y_2O_3 ranging principally from 6 % to 8 %.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Mechanical Property Evaluation and Test Development

Principle Investigators: Douglas T. Smith and Jay S. Wallace, Mechanical Properties Group

Technical Objectives:

The objective of this project is to develop and standardize the procedures and methodology of the instrumented indentation test for hardness and Young's modulus measurements on ceramic coatings.

Technical Description:

The program uses two instrumented indenters (one a commercial nanoindenter and one a NIST-modified microhardness machine) to probe the mechanical properties of bulk materials and thin films. Taken together, the two machines permit indentation studies at peak indentation loads ranging from 40 μN to 40 N, using Vickers, Berkovich and spherical diamond and WC-Co indenter tips. The resulting experimental load-displacement curves are analyzed to yield the hardness and Young's modulus of the material probed, as well as the energy absorbed in the indentation process. Since elastic modulus measurements are sensitive to discontinuities in the microstructure, such as cracks and crack-like voids, they are well suited to the study of changes that occur as a result of changing fabrication conditions or post-fabrication treatments. Relatively small areas of material are probed, permitting local mapping of elastic modulus variations.

The focus of the program is on the development of the *technique* of instrumented indentation, rather than the application of the technique to particular material systems, although data are taken on specific materials of technological interest (*e.g.*, thermal barrier and wear-resistant coatings), as well as candidates for Standard Reference Materials. International workshops, symposia, and round robin standards tests are organized and executed in an effort to guide the instrumented indentation community toward greater standardization in data analysis, to the expand the range of mechanical property characterization possible with the technique, and to develop physical standards for the technique.

External Collaborations:

Collaborations in this work include:

National Physical Laboratory (NPL), U.K., and Tokyo University, Japan: design and execution of VAMAS instrumented indentation round robin testing of model film-substrate systems;

ASTM Task Group E28.06.11: development of ASTM standard test practices and methods for instrumented indentation testing (IIT);

Federal Institute for Materials Research and Testing (BAM), Berlin: development of reference coatings using indentation and spectroscopic ellipsometry;

Praxair Surface Technologies: characterization of TiN and CrN coatings developed as replacements for chrome plating in wear applications;

Institute of Plasma Physics, Academy of Sciences of the Czech Republic: study of processing and property evolution of free standing air plasma sprayed ZrO_2 deposits; and

Department of Material Science and Bioengineering, AIST, MITI, Japan: study of functionally graded materials prepared by plasma arc sintering.

Planned Outcomes:

Recommended guidelines for instrumented indentation testing and analysis procedures, bulk and film standard reference materials, and ASTM standards will be established.

Accomplishments:

In collaboration with the National Physical Laboratory in England and Tokyo University, a new VAMAS Technical Working Area was started in FY 1997 (TWA 22: Mechanical Properties of Thin Coatings), and the first project (Hardness and Modulus Measurement Using Depth Sensing Indentation) is now well under way. Sets of film/substrate specimens have been distributed and tested, and results are being analyzed. In addition, a new project is about to begin on thin film adhesion testing.

The second year of a three year collaboration with BAM on the development of reference coatings has been completed. Dr. Uwe Beck of BAM was a guest scientist at NIST for five months in 1997, working with Dr. Douglas Smith to characterize several candidates for a possible joint NIST/BAM reference coating system for mechanical and optical applications. Coatings of SiO_2 and Si_3N_4 in 0.1 μm and 1.0 μm thicknesses, as well as an SiO_2/Si_3N_4 multilayer, were studied in detail using nanoindentation, x-ray diffraction and spectroscopic ellipsometry, and were found to be promising as potential standard reference systems. Dr. Smith continued the work with a two month visit to BAM in 1998 as a guest scientist. In the final year, residual stress and adhesion of the BAM coatings will be studied.

Extensive measurements of the mechanical properties of several zirconia air plasma sprayed thermal barrier coatings have been made, studying both the influence of feedstock powder characteristics as well as the response of the deposit to thermal treatments. The focus of the work was correlation of elastic modulus changes, measured by instrumented indentation, with microstructural changes, measured with scanning electron microscopy (SEM) and small angle neutron scattering (SANS). Direct SEM observations showed that the fine cracks which were within splats were the first to heal during annealing. The removal of these cracks resulted in a large increase in measured elastic

modulus with only minor changes in the density of the deposit. These observations have been confirmed by SANS measurements. Also, preliminary measurements have shown that, as long as the feedstock particles are melted during deposition, the properties of the deposit are primarily controlled by the mean particle size and are relatively insensitive to the width of the particle size distribution.

One symposium on mechanical property testing for coatings was held as part of the International Conference on Metallurgical Coatings and Thin Films, April, 1998, in San Diego. Another is currently being organized for April, 1999. An ASTM workshop on the technique was held on November 4, 1998, at an ASTM meeting in Norfolk, VA.

Publications:

U. Beck, D.T. Smith, G. Reiners and S.J. Dapkunas, "Mechanical Properties of SiO_2 and Si_3N_4 Coatings: A BAM/NIST Cooperative Project," *Thin Solid Films (in press).*

J. S. Wallace and J. Ilavsky, Elastic Modulus Measurements in Plasma Sprayed Deposits. *Journal of Thermal Spray Technology (in press).*

A.J. Allen, J. Ilavsky, G.G. Long, J.S. Wallace and C.C. Berndt, "Microstructural Changes in YSZ Deposits During Annealing." Submitted to *Proceedings of United Thermal Spray Conference.*

H. Boukari, A.J. Allen, G.G. Long, J. Ilavsky, J. Wallace, C.C. Berndt and H. Herman, "The Role of Feedstock Particle Size on the Microstructural Behavior of Plasma-Sprayed YSZ Deposits During Annealing." Submitted to *Proceedings of United Thermal Spray Conference.*

PROGRAM NAME: Ceramic Coatings

PROJECT TITLE: Modeling of Coating Microstructure and Failure

Principal Investigators: Edwin R. Fuller, Jr., Andrew R. Roosen, Stephen A. Langer [Mathematical and Computational Sciences Division (891), ITL], W. Craig Carter, and Jay S. Wallace

Technical Objectives:

This research is designed to develop models of micro-mechanical behavior, fracture, deformation, damage, and other nonlinear phenomena, in real and simulated microstructures of ceramic coatings. A technique for obtaining the average linear response from selected microstructural regions is envisioned, thereby providing local and bulk properties. Predictions of properties for simulated microstructures and digital representations of actual microstructures (with subsequent comparison to measured properties) are a primary goal. Efficient storage and microstructural representation techniques are to be developed.

Technical Description:

This research models the mechanical and physical behavior of heterogeneous microstructures of ceramic coatings at the microscopic level and develops computationally efficient algorithms and computational codes for simulating the micro-mechanical behavior of these materials. New methods are developed to simulate concurrent physical phenomena in realistic coating microstructures. Elasticity and thermal expansion induced residual stresses in the complex microstructures of air-plasma sprayed thermal barrier coatings are explored *via* computer simulations using both actual and simulated microstructures. In particular, local elastic properties, including elastic anisotropy, and the influence of surface roughness and thermally grown oxide interlayers on residual stresses are investigated. Fracture simulations in these microstructures have also been conducted, but this work is in the early stages.

External Collaborations:

This research involves numerous external collaborations. Informal joint projects include:

Drs. Chun-Hway Hsueh and Paul Becher, Metals and Ceramics Division, Oak Ridge National Laboratory, on the influence of bond-coat roughness and the thermally grown oxide interlayer on residual stresses in air-plasma sprayed thermal barrier coatings;

Prof. Wolfgang Pompe and Stefan Lampenscherf, Institut für Werkstoffwissenschaft, Technische Universität Dresden, Dresden, Germany, on residual stresses and fracture simulation for model thermal barrier coating systems; and

Prof. Chuanshu Ji and Robert Derr, Department of Statistics, University of North Carolina, Chapel Hill, NC, on the development of new statistical tools for generating and quantifying microstructural features.

Planned Outcome:

Computationally efficient algorithms for simulations of the microstructural development in these materials, will be developed.

A model will be developed to describe the influence of pore morphology (elliptical aspect ratio) and pore texture (elliptical orientation) on the average elastic behavior of coatings. Current understanding, based on effective medium theory, often over-estimates the effect since interaction terms between pores are not included.

Plasma sprayed coatings typically have a rough interface between the ceramic overcoating and the metallic bond coat. Computer simulations using actual and simulated microstructures will be established to model the influence of the residual stresses on coating reliability.

Accomplishments:

An object-oriented finite element code (***OOF,*** see Mechanical Properties of Brittle Materials program, "Mechanical Property Modelings") was used to study both simulated and actual coating microstructures. Averaged elastic properties of thermal barrier coatings were calculated on a microstructural basis from digitized images and compared with experimental measurements. Computational simulations were performed on random regions from a micrograph of polished sections of a zirconia plasma sprayed coating. Both plan and section views were considered. Elastic properties were treated as orthotopic in the plane. Experimental measurements were performed *via* Hertzian indentation with a spherical indenter on an instrumented micro-hardness machine. The specimen area sampled for both the simulations and the experiments was approximately 0.01 mm^2.

Simulation studies of the influence of pore morphology and pore texture on the average elastic behavior were initiated. Thus far, elastic properties of media containing a random distribution of elliptical pores of varying volume fractions have been examined. Effective Young's moduli were found to be independent of the bulk Poisson's ratio, and effective Poisson's ratios were found to approach a common value as the volume fraction of pores was increased to the percolation threshold.

During plasma-spraying, adherence of the ceramic overcoat is strongly dependent on roughness of the underlying metallic bond coat. However, the resulting interfacial asperities modify the residual stresses that develop in the coating system due to thermal expansion differences, and other misfit strains, and can generate stresses that induce progressive fracture and eventual spallation of the ceramic coating. For a flat interface, the residual stress is parallel to the interface, as the stress normal to the interface is zero. However, the residual stress normal to the interface becomes non-zero, when the interface has a rough morphology. Computer simulations have been initiated using

OOF with a digitized representation of an actual microstructure of a plasma-sprayed thermal barrier coating (TBC) to give an estimate of the localized residual stresses. Additionally, model TBC microstructures have been examined to evaluate the manner in which the topology of interfacial asperities and the thickness of the thermally grown oxide influence residual stresses.

Publications:

C.H. Hsueh, P. F. Becher, E. R. Fuller, Jr, S.A. Langer, W.C. Carter, "Surface-Roughness Induced Residual Stresses in Thermal Barrier Coatings: Computer Simulations", in proceedings of the 5th International Symposium of Functionally Graded Materials, FGM '98, accepted.

C.H. Hsueh, P. F. Becher, E. R. Fuller, S.A. Langer, and W.C. Carter, "Analytical and Numerical Analyses for Two-Dimensional Stress Transfer", submitted to Mater. Sci. Eng.

C. H. Hsueh, J. A. Haynes, M. J. Lance, P. F. Becher, M. K. Ferber, E. R. Fuller, Jr., S. A. Langer, W. C. Carter, and W. R. Cannon, "Effects of Bond Coat Surface-Roughness on Residual Stresses of Thermal Barrier Coating Systems," submitted to J. Am. Ceram. Soc.

PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Processing/Microstructure Relationships

Principal Investigators: Andrew J. Allen and Gabrielle G. Long

Technical Objectives:

The objectives of this research are to develop techniques for the microstructural analysis of plasma sprayed ceramic coatings, to characterize the anisotropic microstructure as a function of the spray process parameters, and to relate subsequent microstructural evolution both to the service conditions and to the coating properties.

Technical Description:

A combination of Porod small-angle neutron scattering (SANS) and multiple small-angle neutron scattering (MSANS) studies is revealing, and quantifying, the three void structures that govern the properties of plasma sprayed ceramic coatings: anisotropic distributions of cracks within the splats and interlamellar pores between them, together with a wide size distribution of globular and large tetrahedral pores. The effects of several spray process parameters and post-processing variables have been explored for both gray alumina and yttria stabilized zirconia (YSZ), thick, free-standing specimens that were removed from their substrates. Some of the microstructural effects are also being related to the mechanical properties. In addition, methods are being explored to extend some of these studies to thin deposits attached to substrates.

External Collaborations:

Hacene Boukari , University of Maryland, J. Ilavsky, Institute of Plasma Physics, Prague, C.C. Berndt and H. Herman, SUNY/Stoney Brook, and A.N. Goland, Brookhaven National Laboratory are collaborating with the Ceramics Division on the processing-microstructual relationships.

Planned Outcome:

Quantitative assessments will be conducted to show the microstructures of plasma sprayed ceramic deposit coatings can be controlled by the spray-process parameters and how these microstructures respond to the service life conditions.

Accomplishments:

The properties of plasma sprayed ceramic deposit coatings are dominated by the component void morphologies. Our anisotropic multiple small-angle neutron scattering (MSANS) analysis has been previously combined with anisotropic Porod scattering studies, and with density measurements, to determine the volume fractions and surface areas of all three void populations within the deposits,

the mean opening dimensions and anisotropies of the intra-splat cracks and inter-splat lamellar pores, and the mean globular or tetrahedral pore dimension. These studies have now been further combined with anisotropic elastic modulus measurements to obtain the mean planar (penny) diameter of the cracks and lamellar pores. This completes a set of representative microstructural parameters that can be the input for numerical models of the deposit microstructures from which the properties can be predicted.

Our studies of the effects of thermal cycling on the microstructure of YSZ deposits, as a function of the feedstock morphology, have been extended to explore the effects of feedstock particle size distribution. A widely used commercial feedstock powder was differentially sieved to provide three particle size distributions with mean sizes of 32 μm, 47 μm, and 88 μm. The as-received powder was also used for which the somewhat broader particle size distribution had a mean size of 56 μm. Deposits were sprayed from these four feedstock powders with the same feedstock feed rate (0.42 kg/s) and other spray conditions such that all of the particles melted during spraying. Surprisingly simple monotonic (controllable) relationships between the component void population parameters and the feedstock mean particle size have been revealed, with the surface area components showing virtually no change with feedstock particle size. These trends remain for the partially sintered microstructures after thermal cycling the samples at either a modest 1100 °C or at a more elevated 1400 °C. Furthermore, the results for the deposit made from the broader ensemble size distribution of the as-received powder are consistent with these monotonic variations, as defined in terms of mean feedstock particle size. This suggests that feedstock particle size may be one way in which plasma sprayed ceramic deposit microstructures could be designed for specific applications, provided all of the feedstock particle are melted during spraying.

Our previous *in situ* SANS Porod scattering studies of the anisotropic void surface area distributions within plasma sprayed ceramic deposits, using a specially designed high-temperature furnace, have now been augmented by *in situ* MSANS studies to determine the corresponding volumetric and size information. A preliminary analysis of the new data confirms that a preferential sintering out of intra-splat cracks occurs at surprisingly low temperatures (800 °C), and a partial sintering out of inter-lamellar pores occurs over only a few hours at 1200 °C -1400 °C. The implications of this work are significant, given that current jet and gas turbine operating temperatures are in the 1100 °C - 1200 °C range, with future applications likely to require higher temperatures.

While our studies of thick, self-supporting, plasma sprayed ceramic deposits are exploring the generic relationships between microstructure and process variables, and between microstructure and deposit properties, it is essential to determine how far these relationships extend to thin coatings (less than 200 μm thick) on substrates. To this end, we have continued development of grazing-incidence SANS studies, employing a surface reflection geometry with the grazing angle just above the critical angle. A grazing-incidence SANS stage has now been built and tested, and we have been refining our analysis of the anisotropic SANS data generated with this instrument geometry. These improvements, together with preliminary neutron reflectometry measurements to define more precisely the critical incident grazing angle for total neutron reflection at the surface of the coatings actually studied, have enabled us to recover total void surface area values to within 10 % of those

obtained by conventional SANS on the same materials. We have also confirmed the viability of carrying out measurements with a mean depth sensitivity of 30 μm and a maximum depth sensitivity of 150 μm - 200 μm, suitable for studies of aeronautical or gas-turbine thermal barrier coatings.

Publications:

J. Ilavsky, G.G. Long, A.J. Allen, C.C. Berndt and H. Herman; "Changes in the Microstructure of Plasma-Sprayed Yttria-Stabilized Zirconia Deposits During Simulated Operating Conditions," in *'Thermal Spray: A United Forum for Scientific and Technological Advances'* Ed. C.C. Berndt. ASM International, Materials Park, OH, pp 697-702 (1997).

J. Ilavsky, G.G. Long, A.J. Allen, M. Prystay and C. Moreau; "Anisotropic Microstructure of Plasma-Sprayed Deposits," in *'Thermal Spray: Meeting the Challenge of the 21st Century'* Ed. C. Coddet. ASM International, Materials Park, OH, pp 1577-1582 (1998).

J. Ilavsky, G.G. Long, A.J. Allen; "Evolution of the Microstructure of Plasma-Sprayed Deposits During Heating," in *'Thermal Spray: Meeting the Challenge of the 21st Century'* Ed. C. Coddet. ASM International, Materials Park, OH, pp 1641-1644 (1998).

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PROGRAM TITLE: Ceramic Coatings

PROJECT TITLE: Thermal Properties of Ceramic Coatings

Principle Investigators: Eduardo J. Gonzalez, B. Hockey, J. Ritter, Grady S. White, and Daniel Josell (Metallurgy Division)

Technical Objective:

This research is designed to identify those microstructural features in ceramic films that are important for the performance of thermal barrier coatings. This study uses Al_2O_3 on Inconel substrates and ZrO_2 on AlN substrates as model coating systems. To study the scattering effects of interfaces, multilayers of Al_2O_3/Mo and Al/Ti are also investigated.

Technical Description:

Model ceramic films are prepared using a continuous-dip coating technique developed at NIST. This automated technique involves dipping a substrate in an aqueous nitrate solution of the appropriate metal ion and passing the substrate through a furnace held at a temperature between 500 °C and 1000 °C to produce the chosen oxide ceramic. This procedure is repeated until the desired thickness is reached. The microstructure of the films is studied in the optical microscope, scanning electron microscope (SEM), and transmission electron microscope (TEM). Detailed microstructural features are related to observed changes in thermal diffusivity.

Multilayer thermal barrier coatings (TBCs) are prepared by electron beam evaporation of Al_2O_3/Mo bilayers onto Mo substrates and Al/Ti bilayers onto Si substrates. The thermal diffusivities of these multilayer systems are measured and compared to values observed for bulk specimens. Differences are associated with the interfaces between layers, or with other bulk microstructural features, such as grain size, density, and crystallinity.

Thermal diffusivity measurements are conducted using the photothermal deflection technique. This technique uses an intensity-modulated argon-ion laser beam (4 μm to 6 μm in diameter) as a localized heating source on the surface of the sample. The modulated laser beam induces the formation of transient heat pulses, or thermal waves, that diffuse through the specimen. These thermal waves are also generated in the air near the surface of the sample. Thermal waves are probed with a He-Ne laser beam reflected from the surface of the specimen at an angle less than 5° from the plane of the specimen surface. The reflected beam passes through the air just above the heated region of the specimen. A quad-cell photo-diode position sensitive detector monitors the deflection of the probe beam that results from its passage through the thermally induced index of refraction gradient above the heated specimen. The deflected beam is measured as a function of position of the heating beam and the data are compared to the theory of 3-D heat diffusion in a solid. The fitting routine uses a multiparameter least-squares procedure. The thermal diffusivity values have a relative standard uncertainty of less than 10 %, as determined from calibration experiments

with high purity single crystal silicon. Since the thermal diffusion length can be controlled by adjusting the frequency of the heating laser, the sampling volume of material can also be controlled, and, in principle, can be reduced to a few micrometers in diameter at high modulation frequencies. This technique, therefore, has a high spacial resolution which makes it suitable for the characterization of thin films.

Planned Outcomes:

The thermal diffusivities of two model ceramic coating systems will be determined as a function of selectively prepared microstructural characteristics. These results will be used to develop a better understanding of microstructural features that affect thermal transport in ceramic films and multilayer thermal barrier coatings in general. The current understanding of the effects of interfaces as effective phonon scattering boundaries will be improved.

Accomplishments:

Films of α-Al_2O_3, 4 μm to 6 μm thick, have been prepared using the continuous-dip coating technique. The as-deposited films on an Inconel 600 substrate, are amorphous and exhibit a thermal diffusivity of (0.0033 ±0.0004) $cm^2\ s^{-1}$, a value comparable to window glass. The films were crystallized by heat treatment. The thermal diffusivity of the films increased as the films became more crystalline. However, on heat treatment, they also developed porosity which limited their thermal diffusivity to (0.034 ±0.0022) $cm^2\ s^{-1}$. It was determined that crystallinity and residual porosity dominate the resistance to heat flow in these films.

ZrO_2 coatings were deposited on AlN substrates by the dip-coating method. The coatings had a crystalline and complex columnar grain structure. Anisotropic heat flow in these coatings, where the thermal diffusivity along the plane of the film is approximately half the thermal diffusivity through the thickness, was identified. This anisotropy was tentatively attributed to the columnar grain structure present in the films. In-plane heat flow was disturbed by the large number of grain boundaries had to be crossed along this direction. Heat flow through the film thickness essentially occurred across a smaller number of grains.

Thermal diffusivity measurements conducted on the Al_2O_3/Mo multilayers revealed values of thermal diffusivity much lower than the thermal diffusivity of the individual constituents. This result initially suggested that there was a significant interfacial thermal resistance effect. However, it was determined subsequently that the density of the Al_2O_3 layers was sufficiently low that it too limited the heat flow. Consequently, the thermal resistance imposed by the interfaces could not be established unambiguously.

This difficulty was not encountered in the study of Al/Ti multilayers. In this case, each individual layer was fully dense while the observed thermal diffusivity was less than the diffusivity of either constituent. This result was clearly indicative of an interfacial resistance effect.

Publications:

E. J. Gonzalez, B. Hockey, and J. J. Ritter, "Microstructural Development and Thermal Diffusivity of Al_2O_3 Thin Films Prepared by a Continuous Dip-Coating Process", J. Mater. Res., submitted.

CERAMIC MACHINING

The Ceramic Machining Program was established in response to a comprehensive survey of the U.S. advanced ceramics industry indicating that the high cost of machining and, at times, uncertain reliability associated with machining damage were significant impediments to more widespread use of advanced ceramics. This program is designed to address generic industry needs for improved machining technology to be utilized in the manufacture of reliable and cost-effective ceramic components. This is achieved primarily through the development of critical measurement methods, data, and standards.

Specific projects include: (1) effects of abrasive machining on mechanical properties of ceramics, (2) intelligent machining of ceramics, and (3) abrasive finishing and wear of dental ceramics. Materials studied in these projects include ceramics for structural applications such as silicon nitride, and ceramics used for dental restorations such as machinable glass ceramics. The first two projects are conducted jointly with the 20 member Ceramic Machining Consortium. The Consortium members, representing a broad spectrum of industry consisting of materials producers, machine tool builders, suppliers of expendables (such as grinding wheels and fluids), and end users participate by providing materials, testing, and other in-kind contributions. The consortium members also assist NIST in formulating the overall scope of the research projects and contribute to the detailed planning of related experiments. The close working relationship developed between industry, academic institutions, and NIST not only insures the relevance of the research projects but also promotes an efficient and timely transfer of research information to industry for implementation.

PROGRAM TITLE: Ceramic Machining

PROJECT TITLE: Abrasive Finishing and Wear of Dental Ceramics

Principal Investigators: Said Jahanmir and Lewis Ives

Technical Objectives:

The purpose of this research is to assess the influence of machining damage on the strength and wear of dental ceramics.

Technical Description:

The use of ceramics for dental restorations has been on a rapid rise in recent years due to their desirable aesthetics, good durability, and proven biocompatibility. The conventional approach in preparing ceramic restorations, for example crowns, consists of first taking an impression of the clinically prepared tooth, and then preparing a mold which is used to produce a casting of the restoration. The casting is then shaped to specified dimensions by grinding and polishing. As a final step, the dentist finishes the contacting surfaces with a dental handpiece to achieve a precise fit. This sequence of events is time consuming and expensive. In a recently developed procedure, the dental restoration is prepared by machining instead of casting. Application of machining to ceramics, however, requires data and information on machinability as well as on the effects of machining on strength, wear resistance, and contact fatigue. Most clinical failures of restorations have been observed to result either from processing defects in the material or damage produced by machining and/or wear.

External Collaborations:

This project is an integral part of a larger program funded at the University of Medicine and Dentistry of New Jersey by the National Institute of Dental Research to evaluate the relationship between the microstructure of dental ceramics and their performance with respect to machinability, wear resistance, and mechanical properties. NIST (S. Jahanmir and Lewis Ives, Ceramics Division and B. Lawn, MSEL) is participating in this program with the University of Maryland at College Park (Departments of Mechanical Engineering and Materials Science), the University of Maryland at Baltimore (Department of Restorative Dentistry), and the Naval Dental School (Department of Prosthodontics). In addition, four companies (Corning, Inc.; Vita Zhanfabrik; Norton; and Kurary) participate by providing dental ceramics for the investigations.

Planned Outcome:

This project will provide guidelines for microstructural design of dental ceramics to optimize performance based on wear of the restoration and enamel, and guidelines for proper selection of machining parameters for use in abrasive finishing processes by dental technicians and dentists.

Accomplishments:

Evaluation of the damage generated in tooth enamel and dental ceramics by abrasive finishing based on results from a laboratory test device and from experiments conducted by a dentist under conditions typical of clinical practice, clearly suggests that (1) the influence of bur grit size on removal rate is highly sensitive to materials factors such as hardness, toughness, and microstructure, (2) coarse diamond burs do not necessarily result in a higher removal rate than fine burs, (3) coarse burs produce a substantial amount of microcrack damage and chipping in enamel and dental ceramics, and (4) finer diamond burs must be used to remove the damage produced by the use of coarse burs.

The abrasive finishing response of a number of dental restorative materials used to prepare crowns, bridges, and inlays was investigated. The materials included glass-infiltrated aluminas and spinels, a porcelain, a zirconia, several composites, and a series of mica-containing glass ceramics heat treated to systematically vary the microstructure. An instrumented apparatus incorporating a dental handpiece was used to conduct the finishing studies. With this apparatus it was possible to control the applied load, select coolant flow rate, vary bur rotational speed, and measure and collect data on grinding forces. Experiments were carried out with commonly used diamond grit burs with grit sizes ranging from ultrafine (10 μm) to supercoarse (181 μm). Material removal rate, surface finish, and edge chipping were investigated under selected test conditions. As a general observation, removal rate decreased with increasing material hardness, varying by nearly a factor of 100, comparing a relatively hard material such as glass-infiltrated alumina with a softer material such as machinable glass ceramic. Where the difference in hardness was not so large, a positive correlation between hardness and removal rate was not necessarily obtained. For example, the removal rates for a several glass ceramics was equal to or greater than the removal rates obtained for softer polymer matrix composites. Microstructure and toughness apparently had a stronger influence on removal rate than hardness in the latter cases.

For hard materials, the removal rate increased substantially with increasing bur grit size. For softer materials this was not necessarily the case. For a machinable glass ceramic, similar removal rates were realized with coarse and fine grit burs.

On the other hand, for all of the materials studied, both soft and hard, surface roughness increased with increasing grit size. Similarly, edge chipping, which is closely associated with subsurface damage, was greater for coarse grit burs than fine grit burs. The amount of edge chipping for a given grit size, however, was a complex function of hardness, toughness, and microstructure.

Observation of edge chipping and subsurface damage in dental ceramics prepared with diamond burs suggests that human tooth enamel will almost certainly respond in a similar way. Using a recently developed "bonded-interface" technique for subsurface damage evaluation the effect of abrasive machining on tooth enamel was studied. Human third molars were sectioned, carefully polished and cemented together. These bonded-interface specimens were machined and then separated by

dissolving the cement. The polished surfaces were examined using both light microscopy and scanning electron microscopy. Four clinical diamond burs (coarse, medium, fine, and superfine) were used sequentially in a dental handpiece. Tooth preparation with the coarse diamond burs produced relatively large median type cracks in enamel. Finishing with fine diamond burs was effective in crack removal. Therefore, the use of fine diamond burs must follow coarse burs to prevent premature fracture of teeth as a result of relatively large subsurface cracks produced by clinical tooth preparation.

Wear experiments were conducted using a pin-on-disk tribometer. The tests were conducted in distilled water with parameters (e.g., load, speed, sliding distance, etc.) selected to simulate typical oral conditions. Examination of the wear scars on the samples and of the wear debris by scanning electron microscopy indicated that wear of glass-ceramics was dominated by a microfracture mechanism initiated either along cleavage planes of mica or at weak mica-glass interfaces. As the size of the mica platelet increased, wear rate also increased. Since there exists a trade-off between machinability and wear performance, the microstructure must be optimized to obtain restorations with a high machinability rating and at the same time a suitably high wear resistance.

Wear experiments were also conducted on a series of composites containing glass particles in a polymeric matrix. The composites differed with respect to type, size, and type of filler particles. Deformation of the polymer matrix and tribochemical reactions between the filler particles and water were found to have a pronounced influence on wear. The abrasive machining behavior of these composites, however, was controlled mainly by a microfracture process, similar to the glass ceramics. Therefore, the relationship between machinability and wear for these composites differed from that observed for the glass ceramics. This suggests that chemical aspects must be considered in addition to mechanical and microstructural factors when seeking to optimize a polymer composite for machining and wear response.

A series of experiments have been conducted to investigate the influence of machining damage and surface roughness on the wear behavior of dental ceramics. Zirconia specimens were prepared by grinding with a range of grit sizes corresponding to those typically used in finishing dental restorations. For applied loads of 10 N and 20 N, wear rate increased with increasing grit size used to finish the surfaces. This effect, however, was sustained only while the roughened/damaged zone created during finishing still was present. For a load of 30 N similar results were obtained with fine abrasive grit sizes. When finishing was done with coarse abrasive grit (e.g. 163 μm), subsurface damage resulted in a severe microfracture mode of wear. This mode of wear appeared to be self sustaining and was not limited to the original zone of damage.

Publications:

H. H. Xu, J. R. Kelly, S. Jahanmir, V. P. Thompson, and E. D. Rekow," Enamel Subsurface Damage due to Tooth-Preparation with Diamonds," Journal of Dental Research, 76 (1997) 1698-1706.

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H. H. K. Xu and S. Jahanmir," Effect of Microstructure on Damage Tolerance in Grinding Micaceous Glass-Ceramics," Journal of Materials Research, 13 (1998) 2231-2236.

V. S. Nagarajan, B. Hockey, and S. Jahanmir, "Contact Wear Mechanisms of a Dental Composite with a High Filler Content," J. Mat. Science, (1998) in press.

PROGRAM TITLE: Ceramic Machining

PROJECT TITLE: Effects of Abrasive Machining on Mechanical Properties of Ceramics

Principal Investigators: Lewis Ives and Said Jahanmir

Technical Objective:

The objective of this project is to assist industry in the development of machining technology for the manufacture of reliable and cost-effective components made from advanced ceramics. This is accomplished by providing measurement methods and data to assess the influence of damage produced by high-rate machining on properties and performance of ceramics.

Technical Description:

Advanced ceramics are being increasingly used in automotive, aerospace, and manufacturing applications due to their excellent wear and corrosion resistance. Examples include fuel injector components, cutting tools, bearings, and seals. Although ceramics have attractive mechanical, thermal, and chemical properties, high machining costs and sometimes an uncertain reliability due to machining damage are obstacles to more wide-spread use. Specific tasks during the reporting period consisted of the following: (1) effects of grinding on strength of silicon nitride, (2) influence of finishing methods on strength and contact fatigue of silicon nitride, (3) measurement of inter- and intra-laboratory strength variations associated with grinding, and (4) standard test method for assessment of the effects of machining damage on strength. These tasks were carried out jointly with members of the Ceramic Machining Consortium. The Consortium members provide in-kind contributions consisting of ceramic materials, diamond grinding wheels, sample preparation, and testing, as well as input on project selection and planning.

External Collaborations:

Industrial and academic organizations participate in this project by joining the Ceramic Machining Consortium and signing a CRADA for joint research on specific research tasks. Members of the Consortium during the past year included: Cabot Corp.; Ceradyne, Inc.; Chand Kare Technical Ceramics; Cincinnati Milacron, Inc.; Eaton Corporation; Ford Motor Company; General Electric Company; Heraeus Amersil; Landis / Western Atlas; Norton Company; Stevens Institute of Technology; Torrington Company; University of Delaware; University of Maryland; University of Toledo; and West Advanced Ceramics, Inc.

Planned Outcome:

Three major outcomes are expected from this program: (1) recommendations for optimum selection of grinding parameters to be used for specific silicon nitride ceramics, (2) guidelines on finishing methods to obtain damage-free nano-precision surfaces on bearing grade silicon nitride ceramics,

and (3) recommended test procedures for the assessment of the effects of machining damage on strength.

Accomplishments:

A great many—perhaps the majority—of manufactured components are cylindrical or have circular cross-sections. As a consequence, a clear need was identified by the Consortium to develop a test method for determining the influence of surface grinding on the flexure strength of cylindrical specimens. To accomplish this task, a new flexure test fixture for cylindrical specimens was designed and constructed. Initial design verification was accomplished by using strain gauges on specimens and conducting tests on fused silica specimens. The fixture was used successfully to compare the effects of longitudinal and transverse cylindrical grinding on a silicon nitride material. Plans for future studies have been made to determine the influence of a number of important grinding parameters.

Round robin studies to determine the influence of grinding conditions on flexure strength have revealed the existence relatively large experimental variations, both within a single laboratory and between the several laboratories involved. A test exercise was specifically designed to determine the extent of these variations and to reveal its source. Eight Consortium members participated in the exercise. Through careful control of all grinding parameters and conditions it has been possible to obtain a statistical assessment of the size of the variations and to demonstrate that the main source of variation is associated with differences in the grinding wheels. The magnitude of the variation was found to be exacerbated by truing and dressing, but wear associated with normal use of the wheel was also a source of variation.

Development of a standard test method for the assessment of the effects of machining on the strength of advanced ceramics is currently underway under the auspices of ASTM Committee C-28, Advanced Ceramics. The proposed test method is based primarily on the procedures developed and evaluated jointly with the members of the Ceramic Machining Consortium during the past several years. A detailed outline of the standard was presented to Committee C-28 and approved. Writing of a draft was begun.

Rolling contact fatigue life is well known to be sensitive to the presence of surface flaws. An investigation of the influence of machining damage on rolling contact fatigue failure is currently being conducted by members of the Ceramics Machining Consortium. Test specimens of a hot isostatically pressed silicon nitride were prepared using two different finishing methods: chemomechanical polishing (Stevens Institute of Technology), and conventional bearing superfinishing (Torrington). The samples were characterized at NIST for surface roughness and form. The average roughness Ra of the samples finished by chemomechanical polishing was better than 0.004 μm, while the roughness on samples finished by conventional finishing was about 0.027 μm. Rolling contact fatigue testing is currently underway at Torrington Inc. Preliminary results have indicated a somewhat better performance by specimens finished with the chemomechanical polishing method.

Publications:

S. Jahanmir, "Ceramic Machining Research in the United States," Interceram, 46(1997) 90-96.

H. H. K. Xu and S. Jahanmir," Effect of Grinding on Strength of Tetragonal Zirconia and Zirconia-Toughened Alumina," Machining Science and Technology, 1(1997) 49-66.

L. Nelson, H. H. K. Xu, S. Danyluk, and S. Jahanmir, "Subsurface Damage in Grinding Titanium Aluminide," Machining Science and Technology, 1 (1997).

H. S. Ahn, S. Jahanmir, J. A. Slotwinski, and G. V. Blessing, "Detection of Contact Damage in Ceramics by an Ultrasonic Method," J. Materials Research, 13 (1998) 1899-1904.

S. Jahanmir, "Tribology Issues in Machining," Proc. Int. Conf. on Tribology in Manufacturing Processes, Gifu, Japan, October 1997.

PROGRAM TITLE: Ceramic Machining

PROJECT TITLE: Intelligent Machining of Ceramics

Principal Investigators: Said Jahanmir, Mario Cellarosi, and Tze-Jer Chuang

Technical Objective:

The objective of this project is to develop measurement methods, process models, and databases for in-process control and off-line optimization of ceramic grinding to minimize machining damage.

Technical Description:

The current practice in grinding, as applied to ceramics, is labor intensive and operator dependant. Since grinding can introduce surface and subsurface damage in the form of microcracks, residual stresses, and phase changes, operators take a conservative approach, using a "slow" grinding process, which increases the cost of ceramic components. This project is seeking to optimize the grinding process by developing process models for prediction of surface and subsurface grinding damage, neural network analysis for in-process control of ceramic machining, and Ceramic Machining Database.

External Collaborations:

This research is coordinated with the present activities of the NIST Ceramic Machining Consortium. (See "Effects of Abrasive Machining on Mechanical Properties" in the Ceramic Machining Program.

Planned Outcome:

This project is expected to provide a methodology for the intelligent grinding of ceramics, consisting of a PC-based database containing data and information on machinability of advanced ceramics, sensors for monitoring the wheel topography and grinding forces, damage formation models for grinding with wheel topography and grinding forces as inputs, and strategies for on-line modification of grinding parameters to minimize subsurface damage and the resultant low strength.

Accomplishments:

A two-dimensional finite element model was constructed to model the forces produced between the grinding wheel and the work piece in addition to the deformation field and stresses produced in the work piece. The input parameters for the model included both material properties and grinding parameters. The dimensions of the work piece model were selected so that its length in the horizontal direction was several times greater than the length of the cutting zone and that the distance into the work piece was at least ten times larger than the depth of cut. The boundary at the cutting zone was determined based on the wheel size and the velocity ratio. Loading was imposed by

displacements in the cutting zone dictated by the local undeformed chip thickness, which is a function of grinding parameters. For a given set of input parameters, the model predicts the normal and tangential force components imposed by the grinding wheel. The deformation and the stress fields created in the work piece were calculated. The results indicated that, for a sintered reaction bonded silicon nitride, the high shear stresses in the cutting zone could control the mode of failure and result in the formation of microcracks and removal of material by a microfracture process. As expected, the size of the subsurface region subjected to high shear stresses increased with corresponding increase in the depth of cut. As a confirmation of the model, the forces on the work piece computed from the finite element model were compared to measured grinding forces; they were found to be equivalent.

The roughness of a ground surface is an important process response in grinding. Dimensional tolerances, friction, wear, coating adhesion, and appearance can be strongly influence by surface roughness. During grinding, surface roughness is usually controlled by selecting an appropriate set of grinding parameters, in particular wheel grit size, depth of cut, feed rate, and wheel speed. Both spacial distribution and size distribution of grit on the surface of the grinding wheel, however, can have a significant influence on surface roughness. An experimental approach to determining the influence of different grit distributions is not practical. A three-dimensional model of the grinding wheel was developed and used to simulate the grinding process. Heretofore, such simulative studies had been restricted to the use of digitized measurements of the grinding wheel surface, limiting the capability to project the influence of different grit distributions and assess their effect on surface finish. Using the present model, simulated surfaces were generated and compared with actual surfaces. The results were found to be in excellent agreement.

During the past year the database effort was focused on collecting data from the open literature. Based on the availability of information and the requirements for certain types of parameters, a minimum set of required information was determined. After evaluating several hundred publications, about forty references were selected that met the minimum requirements. The data were then examined and verified for errors and inconsistent and/or duplicate data. The evaluated data collected from the literature and those obtained at NIST were compiled into the final version of the Ceramic Machinability Database. This database included about fifty-five fields of information applicable to ceramic grinding including material identification and properties, grinding parameters and conditions, process outputs and results, and references and comments. More than seven-hundred data records (i.e., rows of data) were included in the database. Two versions of the database (Microsoft Access and FoxPro) were distributed to the Consortium members.

A task has been initiated to investigate the relationship between acoustic emission signal characteristics and grinding related processes and responses. The ultimate goal is to utilize the acoustic emission signal together with responses from other sensors to control the grinding process for optimum removal rate with respect to specified requirements for strength and surface finish. One approach will be to employ a neural network modeling technique to arrive at an appropriate algorithm. In a Phase I SBIR project recently completed by N. A. Technologies, the feasibility of using neural network models for the analysis of ceramic machining data was demonstrated. Acoustic

emission hardware was acquired and software written to record and analyze acoustic emission signals during grinding.

CERAMIC PROCESSING

Ceramic products are primarily produced by powder processing, where raw material powders are mixed with forming additives and shaped by various means into green bodies, which are then fired to the final, hardened state. The processing costs can vary greatly depending on the reproducibility and reliability of the process operation. One key to reliable and rapid development of new products is having good test methods to analyze the material at its different stages of processing. Unfortunately, no satisfactory measurements infrastructure yet exists within the ceramics industry, and as a result, much processing relies largely on art and experience. The program on ceramic processing focuses on measurement methods of generic value to all ceramic companies. Clearer definitions are needed as to what needs to be measured, how is it to be measured, and how reliable is the measurement.

The measurement of the physical and chemical properties of powders is an important component of the program. The reliability of various measurement techniques is being assessed in a cooperative international program under the direction of the International Energy Agency and its subtask on ceramic powder characterization which is being coordinated at NIST in the ceramic processing program. In addition, Standard Reference Materials needed to calibrate the measurement instruments in use are being developed. An intramural Advanced Technology Program project on the mechanism of drying, using nuclear magnetic resonance (NMR) imaging, is in progress and is providing direct insight on the moisture gradients formed during drying.

The Ceramic Processing Characterization Consortium (CPCC) was formed in June 1997. Its mission is to assist the U.S. ceramics industry in establishing a generic, powder processing measurements infrastructure. The goal is to assess the measurement needs in ceramics processing and to take all necessary and feasible actions to find viable solutions. Measurement procedures developed are generic and nonproprietary, so ceramic companies can work together to improve the measurement methods of common interest and benefit. The members of the CPCC are volunteers, from companies, instrument makers, universities, and national laboratories. Their contributions to the projects of the CPCC should result in rapid advances in the near future. The current projects are: (1) powder characterization; (2) green body characterization; (3) moisture measurements; (4) dispersion and rheology; and (5) microstructure development. Teams for each of these projects have been formed. The reliability and reproducibility of commonly used instruments will be assessed, new methods will be developed, and a better understanding of how the measured properties affect the behavior of the material at different stages of processing will be developed through basic research studies. All members of the CPCC share in the carrying out the work in the CPCC project teams. The CPCC includes 65 organizations (50 companies, 5 government laboratories, 10 universities).

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE : Ceramic Processing Characterization Consortium

Principal Investigator: Stephen Freiman, Vincent Hackley, Ajit Jillavenkatesa, James Kelly, Lin Sien Lum, Dennis Minor, Patrick Pei, Pu Sen Wang

Technical Objective:

The objective of this project is to establish and enhance a reliable measurements infrastructure for the U.S. ceramic processing industry. Such an infrastructure will potentially benefit a large segment of the ceramic industry by introducing more efficient measurement techniques, reducing processing costs, and increasing product reliability.

Technical Description:

The Ceramic Processing Characterization Consortium (CPCC) was formed at NIST in 1997 with members from the U.S. ceramic industry, analytical instrument manufacturers, academia, and national research laboratories. The consortium is comprised of representatives from 60 companies, 11 universities, and 6 government agencies.

The projects undertaken by the CPCC are of a non-proprietary, pre-competitive nature and applicable to the entire ceramic industry. These projects are: (1) powder characterization; (2) dispersion and rheology; (3) green body characterization; and (4) moisture and drying.

The industrial members of the CPCC help prioritize the measurement needs in ceramic processing. Members of the CPCC actively participate in these projects by evaluating new technologies and instruments on their production lines through well defined field tests; participating in round robin tests, analyses, and surveys; contributing suitable samples and raw materials; and contributing to and reviewing documents and results from CPCC projects.

External Collaborations:

The external collaborators are the members of the CPCC. The members sign a memorandum of understanding agreeing to free exchange and sharing of results and information obtained through the work of the consortium.

Planned Outcomes:

The planned outcomes for the consortium are:

Identification, development, and implementation of improved measurement methods for off-line and on-line, real-time monitoring of ceramic processing variables. Variables such as moisture content,

state of dispersion, primary particle size, and green body density critically influence the properties and quality of the final product;

Development and dissemination of terminology for unambiguous use of technical terms and definitions in scientific literature pertaining to ceramic processing and characterization of processing;

Development of searchable databases and citation indices containing information about raw materials and process control variables used in the processing of ceramic systems;

Formulation and implementation of standardized testing procedures and techniques for characterization of ceramic forming processes; and

Development of reference materials certified for crucial physical and chemical properties that need to be controlled during ceramic processing.

Accomplishments:

The CPCC was formally established in June 1997. Priority areas for research were identified in each of the four research groups. The accomplishments from the projects undertaken by the different groups are:

Successful on-line field tests of moisture determination instruments were conducted. Instruments based on absorption and reflection of near IR radiation by water molecules were tested on regular production lines. One test was conducted at a dinnerware production plant to determine the surface moisture content and local variations in moisture content of the raw material and the green body at different stages of production. Another instrument based on a similar principle, was tested in an advanced materials research lab for characterizing the moisture content, viscosity and binder characteristics of a coating slurry used for automobile engine castings.

Different configurations in which water molecules exist in stoneware clay have been identified using NMR spectroscopy. These configurations vary in the activation energy needed to drive out the water molecules and thus have different the bond structures holding the water molecules in the different configurations.

A nomenclature module for dispersions and suspensions has been developed. This glossary is aimed at alleviating some of the confusion arising due to inappropriate and interchangeable use of terms and definitions.

A searchable citation index for the use of dispersing agents and the parameters of their use is being developed. Search criteria could include author names, trade name or chemical names of dispersing agents and/or materials being dispersed. The structure of this database will enable inclusion of other pertinent information as it is collected or becomes available. Members of the consortium will

contribute to this project by reviewing existing literature and collecting appropriate information for inclusion in the database.

A commercially available instrument based on constant pressure powder envelope pycnometry using has been shown to be comparable to mercury pycnometry, the benchmark technique, for determination of green density. A parametric optimization study of this commercial instrument has identified reasons leading to lack of reproducibility in results commonly observed in industrial applications of this instrument. Other techniques considered in this study include wax-immersion, tap density instruments, oil-displacement, water repellant sprays and geometrical volume and mass techniques.

The viability of non-contact ultrasonic propagation technique to determine the green density of ceramic bodies with simple geometry has been exhibited. Ultrasonic non-contact techniques can provide on-line, rapid, real time, non-destructive analysis, eliminating the need for coupling agents and other associated problems.

A new technique has been developed for visual determination of the state of agglomeration of particles in suspensions. The immense industrial value of this technique has been demonstrated to lie in the technical simplicity, economy and ease of this process. This technique is now being tested by some industrial members of the consortium for possible incorporation into their production processes.

A round robin study was conducted to identify and understand the reasons for observed variations in particle size distributions of powders when measured in different labs. Powders, previously characterized at NIST, were provided to participants with procedures and chemicals for dispersing the powders. The results of the study indicated the crucial need for strict adherence to the prescribed procedures.

The CPCC organized a symposium focussing on issues of ceramic processing characterization, process measurement and control in the ceramic industry. This symposium was conducted at the centennial meeting of the American Ceramic Society. Experts from industry, national labs and academia reviewed and examined the availability and state of modern measurement techniques and procedures for characterization and control of ceramic processing in industries. The proceedings of this symposium will be published by the American Ceramic Society.

Publications:

P. Pei and G. Y. Onoda "Chemical Analysis of Carbon, Nitrogen and Oxygen in Ceramic Powders," to be published in Advances in Ceramic Processing and Control, American Ceramic Society, 1998.

P. Pei and G. Y. Onoda, "Laboratory Techniques for Bulk Density Measurements," to be published in Advances in Ceramic Processing and Control, American Ceramic Society, 1998.

P. S. Wang and G. Y. Onoda, "An Overview of Moisture Measurement techniques for Ceramic Processing," to be published in Advances in Ceramic Processing and Control, American Ceramic Society, 1998.

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE: Development of Powder Characterization Standards

Principal Investigator: James F. Kelly

Technical Objectives:

The primary objective of this work is to develop and certify glass/ceramic powders as particle size distribution standards. A necessary adjunct to this certification is the development of sampling protocols and size measurement procedures.

Technical Description:

The initial work in the development of these Standard Reference Materials is the selection of a powder material with the desired chemical and physical characteristics. These characteristics include size, shape, durability, and reactivity. Industrial sources of powders are identified, test powders are evaluated, and production specifications are developed in cooperation with the powder manufacturer. Procedures have been developed for splitting and bottling of the powder to achieve the necessary level of sample to sample homogeneity. The instrumental techniques utilized for the particle size measurements include optical and scanning electron microscopy, laser diffraction, sieving, sedimentation and electrical zone sensing. The primary techniques are the microscopies because of the direct calibration with NIST line standards.

Planned Outcomes:

Glass bead powders have been obtained and divided for the recertification of the 40 μm to 170 μm glass bead SRM 1004b, and for the new SRM 1021, which will extend the lower range of available glass sphere size distributions standards to 1 μm . The measurement of particle size distribution by laser diffraction has been completed for three zeolite powders. Certification has been completed for Reference Materials RM 8010 for sieving of raw materials in the glass manufacturing industry. Development is under way for a new SRM using a tungsten carbide/cobalt thermal spray material.

Accomplishments:

Spherical glass SRM's 1003b, 1004a, 1017b, 1018b, and 1019b, covering particle size ranges from 15 μm to 2400 μm, are now available to industrial laboratories and test facilities. A spray dried zirconia powder, SRM 1982, has been developed for particle size calibration use in the thermal spray industry. Several thousand units of these materials have been produced and certified for size distribution and homogeneity. Approximately 500 units per year of these size distribution standards are purchased by industry for use in their quality control test programs.

Publications:

RM 8010, Silica sands - Particle Size Distribution, NIST Standard Reference Materials Program (1998)

SRM 1018b, Glass Beads – Particle Size Distribution, NIST Standard Reference Materials Program (1997)

SRM 1019b, Glass Beads – Particle Size Distribution, NIST Standard Reference Materials Program (1997)

SRM 1982, Zirconia Thermal Spray Powder – Particle Size Distribution, NIST Standard Reference Materials Program (1996).

PROGRAM TITLE: Ceramic Processing

PROJECT TITLE: IEA Subtask 10 (Secondary Powder Properties)

Principal Investigators: Lin-Sien Lum and George Onoda

Technical Objective:

The objective of this project is to establish and refine pre-standards procedures for the characterization of secondary properties of ceramic powders.

Technical Descriptions:

There are four focus areas in this international interlaboratory study: 1) state of dispersion of powders; 2) rheology of slurries; 3) properties of spray dried powders; and 4) evaluation of green bodies. Three powders were studied: silicon nitride, silicon carbide, and aluminum oxide, in both the as received and the spray dried granule form. This project (Subtask 10) is a continuation of the previous project (Subtask 8) where initial examination of different methods and instrumentation for the characterization of secondary properties were accomplished. Procedure improvements of selected methods were conducted for Subtask 10.

External Collaborations:

Technical collaborations with international organizations include: BAM (Germany), Swedish Ceramic Institute (Sweden), VITO (Belgium), and JFCC (Japan).

Planned Outcomes:

This project will establish improved and tightened procedures for the following secondary properties: deagglomeration of ceramic powders in slurries; rheological properties; flow rate, size distribution, moisture content, and binder content of spray dried powders; bulk density, porosity, and green strength of green body compacts.

Accomplishments:

A method to determine the state of dispersion of ceramic powders was developed. The method involves following the changes in the particle size distribution as a function of the ultrasonication time used to disperse the powder in dilute suspension. If deagglomeration occurs by ultrasonication, then the particle size distribution should shift toward the finer size as the ultrasonication is increased. The final dispersed state is the size distribution that is attained after no further changes in particle size distribution occurs with longer ultrasonication time.

Measurement procedures have been developed to determine the rheology of ceramic suspensions using a rotational viscometer and a rotational rheometer. The suspensions in these procedures have a solids volume fraction of 30 %. The procedure specify the measurement of apparent viscosity, shear-thinning index and thixotropic response in water-based ceramic powders slurries over a shear rate range roughly 1 s^{-1} to 500 s^{-1}.

Procedures have been developed to determine the flow rate, size distribution, moisture content and binder content of spray dried powders. The procedure for flow rate measurement uses a modified Hall Flow method. A dry sieving technique is used to measure the size distribution of the granules. The moisture and binder content is determined by measuring the weight loss of the powders after drying.

Procedures to determine bulk density, porosity, and tensile strength for green body compacts have been developed. The bulk density is calculated from measurments of the external dimensions and the mass of the compacts . A mercury porosimetry technique is used to determine the porosity of the compacts. The tensile strength of the green body compacts is measured by the diametral compression test. The test consists in compressing a cylindrical specimen diametrically between two flat platens of a universal testing machine. (For further discussion of this test method, see "Mechanical Test Development" in the program title Mechanical Properties of Brittle Materials.)

Different laboratories were responsible for each of the focus areas of the secondary properties. Each of the measurement procedures passed through rigorous robustness testing to tighten the experimental parameters. The technical leaders reviewed the finalized procedures before the procedures were compiled and distributed to the participants. To improve the quality of the spray dried powders used for Subtask 10, commercial sources of the powders were utilized to eliminate problems associated with pilot size spray dryers. Green body compacts were fabricated by VITO (Belgium) from similar spray dried powders for density, porosity, and tensile strength measurements. Round robin studies will assess the repeatability and reproducibility of the measurement methods have been scheduled. Thirty-two participants from five countries will participate in the round robin.

CERAMIC THIN FILM MEASUREMENTS AND STANDARDS

Functional ceramics (*e.g.*, ceramics primarily intended for optical, electronic, or thermal management applications) are increasingly being used in film geometries. In response to this growing segment of the ceramics community, the Thin Film Measurements and Standards Program endeavors to provide improved measurement tools and data that are needed to evaluate advanced ceramic films and film systems. Increasingly critical film performance requirements (*e.g.*, reduced dimensions, increased purity, improved interface properties, increased production rates, and tighter control of properties) place stringent demands on film processing control, models, and characterization techniques. However, lack of measurement methods to monitor film processing and accurately characterize film properties, as well as limited theoretical understanding of interrelationships between processing conditions and final film properties, reduce most film processing to empirical procedures. The activities in this program are designed to address these measurement and modeling issues, both with regard to specific, near term industrial needs as well as to the development of a materials science knowledge base required for use of ceramic films in future applications. Near term and long range goals have been developed based upon both general discussions between Materials Science and Engineering Laboratory staff and representatives of industry and universities at professional meetings and consortia workshops as well as focused, collaborative research projects with specific organizations.

The film characterization techniques in use or under development include electrical, mechanical, optical, thermal, and x-ray measurements. Specific research activities include:

- investigations of the processing and microstructural features that control poling behavior and domain stability in ferroelectric films;
- development and utilization of spectroscopic procedures to evaluate film composition in $BaTiO_3$ and to detect defects in ferroelectric and semiconductor films;
- development of methods to measure and statistically analyze texture and texture distributions in films and to relate these data to processing conditions;
- development of measurement procedures, models, and standards to permit quantitative evaluation of thermal diffusivity in thin films and to relate thermal diffusivity to film microstructure and morphology;
- application of advanced x-ray measurement capabilities (e.g., EXAFS, DAFS) to the analysis of film structure and composition and the construction of an in-house state-of-the-art x-ray facility.
- development of standard measurement procedures and standards for determining film adhesion;

- participation in development of optoelectronic film composition standards for industrial photoluminescence and x-ray instrument calibration

A critical requirement for the projects cited above is the ability to generate model film systems. To this end, this program includes two film deposition capabilities: metalorganic chemical vapor deposition (MOCVD) and pulsed laser deposition (PLD). The MOCVD system is an integral part of the ferroelectric film research projects already listed and, during the past year, has undergone a major upgrade to provide more precise compositional control. The PLD facility has the capability for depositing a wide variety of films under deposition conditions that complement those of the MOCVD system.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Ferroelectric Poling and Domain Stability

Principal Investigators: John Blendell, Lawrence D. Rotter and Debra L. Kaiser

Technical Objective:

The objective of this research is to develop measurement techniques for evaluating ferroelectric domain structure, poling efficiency and domain stability that will assist U.S. industry in the commercialization of ferroelectric oxide thin films for electronic and optoelectronic applications.

Technical Description:

Ferroelectric materials are characterized by the presence of domains, which are regions of uniform crystallographic and electrical polarization. Tetragonal ferroelectrics have two types of domain boundaries: 90° boundaries, in which the *c*-axis in one domain is aligned with the *a*-axis in the adjacent domain; and 180° boundaries, in which the *c*-axis in the adjoining grains are aligned but the polarization is in opposite directions. In films, switching the polarization direction of the 180° domains can be accomplished by applying an electric field, but switching the crystallographic orientation of the 90° domains generally requires application of a mechanical stress.

The domain structure, or arrangement of domains of differing crystallographic orientation and polarization, dominates the properties of ferroelectric oxide thin films and their performance and reliability in integrated ferroelectric nonvolatile memory devices, microelectromechanical systems (MEMs), pyroelectric detectors, and optoelectronic devices. For example, in the case of the memory devices, the individual domains or groups of domains that comprise a single memory cell must switch orientations in a reproducible manner upon repeated read/erase/write operations and, in the absence of a switching field, must be stable over time. For any application, it is necessary to be able to determine the domain structure in the film and to assess the efficiency of switching the polarization and the stability of the polarization state.

Planned Outcome:

This research should provide present and future US industries engaged in ferroelectric oxide thin film device development with appropriate measurement tools to evaluate domain structure, polarization efficiency and domain stability in ferroelectric thin films. In addition, the research will provide a fundamental knowledge base on the microstructure/property relationships relevant to these domain issues.

Accomplishments:

A recently reported technique [A. Gruverman *et al.*, J. Vac. Sci. Tech. B, **14**[2], 602 (1996)] for imaging the polarization of ferroelectric materials based on the piezoelectric response to an applied electric field has been used to observe 180° domains in $Pb(Zr,Ti)O_3$ (PZT) thin films with the polar *c*-axis oriented normal to the $Pt/SiO_2/Si$ substrate. In the measurements, an applied AC electric field (1 MV/m to 10 MV/m) causes changes in the dimension of the ferroelectric film due to piezoelectric behavior. Such changes have been observed by atomic force microscopy and the phase shift of the response is directly related to the orientation of the polarization of the sample. The spatial resolution of the technique is limited to ≈ 20 nm due to the contact area of the tip. The response varies from in-phase response (when the polarization is in the direction of the applied field) to no response (when the polarization is in the plane of the film) to response which is 180° out of phase (when the polarization is in the opposite direction to the applied field). The polarization direction in ≈ 100 nm regions of the PZT film has been switched by applying a larger electric field (50 MV/m to 100 MV/m) through the AFM tip. With this technique, it will be possible to measure the switching field required to change the polarization, and to measure changes in switching field with time or number of cycles. The technique will also be used to study the switching behavior as a function of location in a grain and to look at the changes in switching with cycling over a larger area such as may be representative of a memory cell.

Atomic force microscopy has also been used to image 90° domain boundaries in bulk, poled PZT samples that were mechanically polished and etched in phosphoric acid. The domains were 200 nm to 500 nm in width and the grain size in the samples was 3 μm to 4 μm. The measurements showed that polishing and etching can be accomplished without altering the domain structure in the material. One sample was thermally depoled (*i.e.*, the domain structure was randomized by passing the specimen through the Curie temperature). Interdigitated metallic electrodes were deposited on the depoled PZT sample. The sample was then poled through application of an electric field between the electrodes, and the resulting domain structure was found to be different from the structure in the initial poled state. This poling process also caused microcracking to occur, and the microcracks were observed to propagate across grain boundaries. The microcracks may arise due to stresses associated with changes in the domain structure during poling and can be a source of failure under cyclic electric loading. It was not possible to determine if the cracks originated from grain boundaries, inclusions or domain walls.

Films can contain undesirable secondary phases that change the average strain in the film and thereby influence the orientation of the ferroelectric domains that form during cooling through the Curie temperature after deposition. The orientation of the tetragonal $Ba_{0.94}Sr_{0.06}TiO_3$ (BST) domains in $(Ba_{0.94}Sr_{0.06})_yTiO_{2+y}$ thin films (y = (Ba + Sr)/Ti = 0.34 to 1.64) composed of fine-grained BST and an amorphous phase was measured by conventional θ-2θ x-ray diffraction. The films were deposited on MgO substrates by metalorganic chemical vapor deposition at temperatures of 600 ° C to 800 ° C. High resolution transmission electron microscopy studies showed that the films contained epitaxial BST and an amorphous phase. X-ray diffraction measurements showed

that the BST domains were oriented with either an *a*-axis and/or the *c*-axis normal to the substrate surface. (It is not possible to detect the presence of 90° domains in *a*-axis oriented films by conventional θ-2θ x-ray diffraction.) The domain orientation was found to be strongly dependent upon the film composition: pure *c*-axis for $0.34 \leq y \leq 0.44$, pure *a*-axis for $0.73 \leq y \leq 01.64$ and $y = 0.55$ and 0.63, and mixed *a* and *c* axis for $0.68 \leq y \leq 0.72$. In an attempt to explain these results, average strains in films containing BST and an amorphous phase were calculated assuming that the strain energy is mainly determined by an average misfit between the two phases and the elastically-rigid MgO substrate. In the calculations, the Ti-rich films with $0.34 \leq y < 1$ were assumed to be a mixture of stoichiometric BST ($y = 1$) and an amorphous phase of fixed composition $y_{AP} = 0.33$ (this value was selected because films with $y < 0.34$ were fully amorphous). Tensile misfit strains of +0.68 % in a pure *a*-BST film and +0.89 % in a pure *c*-BST film were calculated at a temperature just below the Curie temperature $T_c = 111$ EC. By assuming a compressive misfit strain of ≈ 1% in the amorphous phase, an analysis of the average strains in the two-phase films yielded a composition dependence for the BST domain orientation that was consistent with the observed dependence for the majority of the Ti-rich films.

Publications:

D. L. Kaiser, M. D. Vaudin, L. D. Rotter, J. E. Bonevich, I. Levin, J. T. Armstrong, A. L. Roytburd, and D. G. Schlom, "Effect of Film Composition on the Orientation of (Ba,Sr)TiO_3 Grains in $(Ba,Sr)_yTiO_{2+y}$ Thin Films," submitted to J. Mater. Res.

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Chemical Standards for Optoelectronics

Principle Investigators: Lawrence H. Robins

Technical Objective:

The objective is to quantify the accuracy limits of the indirect measurement methods currently used by industry to determine the chemical composition of semiconductor films in the technologically important $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As_yP_{1-y}$ alloy systems. This project is one component of a larger NIST compound semiconductor composition standards program, which is a collaboration among four divisions. The overall objective of the larger program is to develop high-accuracy, direct composition measurement methods based on chemical microanalysis, and produce standard reference materials with certified compositions in the selected alloy systems.

Technical Description:

Compound semiconductor manufacturers currently rely primarily on two indirect methods to measure the chemical composition of semiconductor alloy films: photoluminescence (PL) spectroscopy, and x-ray diffraction (XRD) rocking curves. These methods are referred to as indirect because the measured quantities, electronic band gap and lattice constant, are functions of composition, but may also vary with other factors such as temperature or strain. In this project, we will use PL spectroscopy to measure the band gap of samples provided through the NIST composition standards program. We will quantify the accuracy limits of the PL measurements by conducting internal and external round-robin comparisons of preliminary composition reference samples, conducting in-depth studies to resolve discrepancies, and applying related techniques such as cathodoluminescence to reduce uncertainties in the measurements. Specific factors to be addressed are wavelength accuracy, wavelength-dependent spectrometer response correction, peak fitting methods, excitation intensity, sample temperature, low level impurities, and, for InGaAsP, residual strain.

XRD rocking curve measurements are planned on the Ceramics Division's new, high-resolution thin film diffractometer, scheduled to be operational in Spring 1999. Additional factors to be addressed in the XRD measurements are effects of the x-ray optics, goniometer precision, and epilayer tilt.

External Collaborations:

The other NIST research divisions and principal investigators participating in the composition standards program are Kris Bertness, Optoelectronics, Joseph Pellegrino, Semiconductor Electronics, and John Armstrong, Surface and Microanalysis Science. Optoelectronics and Semiconductor Electronics are growing samples by molecular beam epitary and conducting *in situ* characterization,

while Surface and Microanalysis Science is responsible for developing high-accuracy composition measurement methods based on chemical microanalysis.

Planned Outcomes:

Improvements in PL experimental techniques and/or data analysis methods will be developed that reduce the uncertainty and systematic errors in the measured parameter (electronic band gap). These improvements will be demonstrated as reductions in the discrepancies between measurements of the same sample conducted in different laboratories.

An accurate calibration curve will be developed that specifies the band gap of $Al_xGa_{1-x}As$ as a function of composition (x); for the $In_xGa_{1-x}As_yP_{1-y}$ alloy system, accurate band gap values will be provided at several points within the (x, y) composition plane. This outcome is dependent on the success of other goals of the composition standards program, specifically the development of high accuracy primary composition measurement methods.

The improvements in PL analysis and the generation of calibration curves will provide U.S. compound semiconductor industries with information needed to improve the accuracy of routine PL measurements of film composition.

Accomplishments:

Room temperature PL measurements were performed on four $Al_xGa_{1-x}As$ film / GaAs substrate samples grown in the Optoelectronics and Semiconductor Electronics Divisions, all with x close to 0.2. Several significant results were obtained from these initial measurements.

First, the observed PL peak emission energy showed a large shift with excitation intensity, up to 0.04 eV at incident power levels to 0.4 W. This shift is explained by local heating of the sample, due to the small laser spot size and short penetration depth, which leads to a large value of the absorbed power per unit volume. The heating also resulted in a broadening of the PL linewidth, and a change in the exponential slope of the PL spectrum at high energy. The change in the exponential slope was used to obtain a direct estimate of the temperature of the excited sample volume; the temperature increased from the ambient value, 296 K, to greater than 400 K at the highest incident power level. This result indicates that the excitation intensity must be limited to avoid heating above ambient temperature and the resulting bandgap shift, either by limiting the incident power or changing the laser spot geometry (e.g., using cylindrical optics, which focus the beam to a line rather than a point).

Second, strong GaAs (substrate) PL emission peaks were observed from two of the samples (with film thicknesses of 200 nm; the other two samples have film thicknesses of 2000 nm). Because of this observation, the measurement method was modified by defining the primary measured parameter as the difference between the film ($Al_xGa_{1-x}As$) and substrate (GaAs, or x=0 composition) band gaps, rather than the film band gap alone. There are two important advantages to the differential film-substrate measurement method: (a) there is a difficult-to-determine shift between

the directly measured peak PL emission energy and the desired band gap energy; if this shift is the same for the film and substrate emission peaks, as the data suggest, then it is eliminated in a differential measurement; (b) when only the film band gap is measured, then the band gap of pure GaAs (x=0) enters as a parameter in the model equation that relates band gap to composition; the differential measurement eliminates this parameter from the model equation.

Third, published models for the functional dependence of the band gap on composition were used to calculate the film compositions (x) from the measured band gap differences. Twelve different models were found in a review of the $Al_xGa_{1-x}As$ literature, eight based on room-temperature optical or electrical measurements and four based on low-temperature measurements. There is a large discrepancy among the published models; values of x calculated using the various models vary by up to 0.04 for the same measured film-substrate bandgap difference. Compositions of the four examined samples, calculated with each of the twelve published models, are shown below in the figure. The discrepancy among the existing models underlines the need for accurate, direct composition measurements to establish a primary standard for calibration of the indirect (PL and XRD) measurements.

Calculated Al atomic fractions, x, for four $Al_xGa_{1-x}As$ samples, from measured film-substrate band gap differences,E_G, according to each of twelve different published models that state the functional dependence of the band gap on x. The large discrepancy among the various models causes a 4% model-dependent uncertainty in the calculated x value for each film.

Publications:

L. H. Robins, J. R. Lowney, and D. K. Wickenden, "Cathodoluminescence, photoluminescence, and optical absorbance spectroscopy of aluminum gallium nitride ($Al_xGa_{1-x}N$) films," J. Matls. Res. Vol 13 (9), 2480-2497 (1998).

L. H. Robins and D. K. Wickenden, "Spatially resolved luminescence studies of defects and stress in aluminum gallium nitride films," Appl. Phys. Letts., Vol. 71 (26), 3841-3843 (1997).

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: *In Situ* Process Monitoring and Control

Principal Investigators: John W. Hastie, David W. Bonnell, Albert J. Paul, Peter K. Schenck

Technical Objective:

The project seeks to develop molecular-level measurement capabilities needed (a) to monitor, *in situ* and in real time, the pulsed laser deposition (PLD) of thin films and (b) to provide basic data for development of process models for physical and chemical film and coating deposition processes. The measurement methods and process models developed are intended to allow industry to utilize in-process monitoring for characterization of the process, and for optimum control of the resultant thin film properties. These capabilities should reduce the need for time consuming empirical derivation of improved processing conditions and extensive post processing analysis currently used in industry.

Technical Description:

Measurement approaches developed earlier for this project continue to be refined, and include, primarily: time- and angular-resolved molecular beam sampling mass spectrometry (MBMS) coupled with *in situ* deposition rate measurements, multichannel optical emission and absorption spectroscopy, and optical imaging of emission, including particulate transport, utilizing high speed intensified charged-coupled device (ICCD) detection. In addition, an optical reflectometry approach to measurement of film thickness and refractive index is under development using a multichannel fiber-optic-coupled spectrometer. The measurement methods are complemented by process model development based on coupled fundamental processes, including hydrodynamics, thermodynamics, and chemical kinetics. Using the combined real time results of optical spectroscopy, optical imaging and molecular beam mass spectrometry, molecular-level models are being developed and tested for the PLD process. This approach provides for a detailed understanding of the laser interaction with the target and plume, the mode of gas transport to the substrate, and, in addition, the redistribution of species concentrations and energies at the substrate.

External Collaborations:

Collaborations have been developed with the following individuals and groups: Dr. A. Pique, Neocera and NRL for studies of metal sulfide films for optical data storage technology; Dr. D. Chrisey and Dr. J. Horwitz, NRL for PLD Workshop, Dr. P. Ghosh, Indian Institute of Technology, Kanpur, India for Monte Carlo vapor transport model development; Dr. M. Joseph, Indira Gandhi Institute, Kalpakkam, India for laser vaporization mass spectrometry, Dr. V. Stolyarova, Institute for Silicate Research, St. Petersburg, Russia, for development of oxide phase equilibria models and data, and Dr. C. Chatillon, ENSEEG Recherche LTPCM, France and Dr. J. Drowart, Free Univ., Brussells, for development of methods and data for quantifying mass spectrometric data (IUPAC

sponsorship), and Dr. D. Sanders, Lawrence Livermore National Laboratory for applications in e-beam/x-ray generation technology and laser-materials interactions.

Planned Outcome:

Achievement of the technical objectives will allow for improved real time analysis and control of the deposition process during PLD. Reference films, produced under well controlled conditions, to be used by others for film property measurement development, also result from this work.

Accomplishments:

NIST, jointly with NRL, organized a workshop, "Pulsed Laser Deposition Technological Barriers: Research Needs and Opportunities" (see http://amp.nrl.navy.mil/code6670/workshop.html). Nearly one hundred US PLD participants equally represented industry, government laboratories and agencies, and academia. Key discussion areas included materials and applications, measurement and standards issues associated with scale-up, tool and process development, and process monitoring and control, together with supporting fundamental research. While it is clear that PLD provides researchers with a powerful tool for preparing prototype inorganic thin films of chemically and structurally complex materials, which are difficult to produce by other conventional approaches, there remain technological barriers to the adoption of the technique for large-scale production. It appears that the fact that other deposition methods with commercially available tooling appear to offer less risk have limited PLD opportunities in production environments.

A portable fiber-optic-coupled multichannel optical spectrometer has been modified to perform two-dimensional reflectometry on thin films. The system measures the reflectivity of the film-substrate over the wavelength range 350 nm to 900 nm, with a spatial resolution of 1 mm. Two-dimensional maps of the film thickness and index of refraction can be obtained by fitting the spectral data to a model developed by L. Robins and L. Rotter in the Film Characterization and Properties Group. This new capability has been particularly useful in evaluating the performance of the new liquid delivery system in the MOCVD reactor and in confirming PLD models of gas dynamic material redistribution effects.

The PLD facility has been upgraded with a NIST-designed beam delivery system. The new system allows for reproducible location and focusing of the excimer laser on the target and also includes a computer controllable zero-walk-off beam attenuator. Together, these features allow for precision studies of the role of fluence and spot size on the deposition pattern and measured film properties, such as d-spacing, texture (x-ray) and refractive index. The addition of a high vacuum capability was also made for improved process reproducibility and film quality.

In order to model the PLD process with direct inclusion of plume-target and plume-substrate interactions, a 2-dimensional Monte Carlo model, using stochastic sampling with direct computation of molecular collisions, has been developed. This model reproduces quite well the detailed velocity distribution profiles measured downstream by MBMS, and has recently been applied to simulations

of the higher energy optically imaged data. Comparisons have also been made between the hydrodynamic and Monte Carlo models, leading to an explanation of a prior discrepancy between model and experimental film compositions for $BaTiO_3$. The observed deposition uniformity apparently results from the formation of transverse flow in a boundary layer at the substrate that compensates for hydrodynamic Mach focusing along the centerline of species with higher molecular weight.

Publications:

A.J. Paul, P.K. Schenck, D.W. Bonnell, J.W. Hastie, M.D. Vaudin, "The effect of Gas-Surface Interactions on Laser-Generated $BaTiO_3$ Plumes during PLD," *Advances in Laser Ablation of Materials, MRS Symp 526*, R.K. Singh, D.H. Lowndes, D.B. Chrisey, J. Narayan, T. Kawai, E. Fogarassy, Eds., (MRS, Pittsburgh, PA, 1998April, Spring 1998 MRS Meeting)

V. Stolyarova, S. Shornikov, M. Shultz, J.W. Hastie, and D.W. Bonnell, "Thermodynamic Properties of the Al_2O_3– SiO_2 System: Assessment and Predictions Using a Complex Liquid Model," *High Temp. and Matls. Sci*, 1998.

J.W. Hastie, D.W. Bonnell, D. Chrisey, J. Horwitz, "Laser Deposition Holds Promise, Needs Development," *Laser Focus World*, Vol. 34 (9). 19 (1998).

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Optical Characterization Techniques

Principle Investigators: Lawrence H. Robins, Albert Paul, Lawrence D. Rotter

Technical Objective:

The objective is to develop and use optical characterization techniques for the measurement of critical properties of thin film and multilayer structures of importance to the photonics and electronics industries, in particular structures that utilize group III nitride or ferroelectric oxide materials in the active layers.

Technical Description:

Measurement techniques including cathodoluminescence (CL) imaging and spectroscopy, photoluminescence (PL) excitation and emission spectroscopy, Raman spectroscopy, transmittance and reflectance mode spectrophotometry, second harmonic generation, polarimetry, and prism coupling are used to determine thin film and substrate properties such as thickness, optical constants, electronic band gap, defect and impurity energy levels, structural and compositional phase content, residual stress/strain, electro-optic constants, waveguiding losses, internal electric fields, and ferroelectric poling efficiency. This year's activities have focussed on the development of techniques to characterize compositional inhomogeneity in group III nitride films for short wavelength photonic devices.

External Collaborations:

Group III nitride films were obtained from J. Ari Tuchman and coworkers at Principia Lightworks, J.C. Roberts, S.M. Bedair and coworkers at North Carolina State University (NCSU), and Dennis Wickenden at the Johns Hopkins University Applied Physics Laboratory (JHAPL).

Planned Outcomes:

Optical measurement methods based on double spectrally resolved PL excitation spectroscopy, and on the excitation intensity dependence of the CL or PL emission spectrum, will be developed to quantify the occurrence of compositional inhomogeneity and phase separation in $In_yGa_{1-y}N$ films and multiple quantum well (MQW) structures.

A model will be developed to predict the luminescence lineshape of highly strained $Al_xGa_{1-x}N$ films as a function of the x-ray diffraction (XRD) lineshape, based on the hypothesis that both lineshapes are due primarily to the inhomogeneous strain distribution and on model equations for the electronic deformation potentials.

These methods and models will provide the optoelectronics industry with measurement tools to quantify inhomogeneous composition and inhomogeneous strain in group III nitride thin films.

Accomplishments:

"Bulk-like" $In_yGa_{1-y}N$ films with nominal compositions from y=0.06 to y=0.49 (from NCSU) were characterized by the following methods: transmittance spectrophotometry, Raman spectroscopy, and double-spectrally-resolved PL excitation spectroscopy. (The y values were determined from XRD lattice constant measurements done at NCSU; the lattice constant increases by 10% from GaN to InN.) The sensitivity of each technique to compositional inhomogeneity was assessed. Previous structural characterization of the films by XRD, transmission electron microscopy (TEM), and selected-area diffraction (SAD) showed that phase separation into indium-rich and indium-poor regions, on a length scale of 10 nm or less, occurred in films with $y \geq 0.26$ but not in lower-indium films.

The transmittance spectrum of each film shows an absorption that increases approximately linearly with energy above a distinct absorption edge. The absorption edge energy decreases as an approximately linear function of y, from 3.1 eV at y=0.06 to 1.6 eV at y=0.43. Comparison of the transmittance data with the literature values of the band gaps of the pure compounds, 3.4 eV for GaN and 1.9 eV for InN, suggests the presence of phases with higher indium content than the nominal composition (y) of the films. However, we did not find a feature of the transmittance spectra that correlates directly with phase separation, such as distinct absorption edges for indium-rich and indium-poor phases within a single sample.

Raman spectra were obtained from films with $y \geq 0.28$. It was not possible to obtain Raman spectra of the films with $y<0.28$ because the Raman signal was overwhelmed by the PL background. The Raman peak shifts to lower wavenumber and broadens with increasing y; the broadening is evidence for compositional inhomogeneity, because the Raman frequency decreases with increasing indium content, due to the large In/Ga mass ratio. There is also a splitting between the Raman peaks excited at 2.41 eV and 2.71 eV, which increases with y. This splitting is ascribed to resonant excitation of different compositional phases at the two excitation energies, and is thus interpreted as a spectral signature of the phase separation.

Double spectrally resolved PL excitation spectroscopy is another technique that is sensitive to the occurrence of phase separation. In this experiment, PL is excited by a wavelength-tunable source, and the intensity of the PL signal within a narrow emission band is monitored as the excitation energy is scanned. The measurement is then repeated for several different emission bands from the same sample, so that a set of excitation spectra is obtained, with each spectrum corresponding to a different emission energy. PL excitation spectroscopy results were obtained for samples with y=0.06 to y=0.43. In the excitation spectrum from each sample and PL emission band, the intensity was observed to increase with increasing excitation energy within a specific energy range; the excitation threshold is defined as the energy corresponding to the midpoint of the increase. In the y=0.06 and y=0.19 samples, the excitation threshold is almost independent of emission energy, while in the

samples with $y \geq 0.28$, the excitation threshold has a strong dependence on emission energy, suggesting that different PL emission bands originate from different compositional phases in the latter samples. These results are consistent with the previous structural measurements (XRD, TEM and SAD), which showed the films with $y \geq 0.26$ are phase-separated while the lower-indium films are homogeneous.

Of the three techniques assessed, PL excitation spectroscopy appears to be the best suited to measurements of compositional inhomogeneity in $In_yGa_{1-y}N$ layers, because there is a distinct "spectral signature" associated with the occurrence of phase separation, and the measurement is applicable within a wide range of compositions. Preliminary results on MQW structures, which will not be discussed in detail here, suggest that still another technique, the excitation intensity dependence of the emission spectrum, may also provide a quantitative probe of phase separation. We plan to compare the latter two techniques in future work.

Residual strain is another microstructural property that has a significant effect on the optical properties of group III nitride films. Strain in (0001) oriented $Al_xGa_{1-x}N$ films with x=0 to x=0.36 (from JHAPL) was characterized by XRD and CL spectroscopies. The 0002, 0004 and 0006 XRD peaks were measured for each film; the full width at half maximum (FWHM) of the XRD peaks was observed to increase with increasing Al fraction (x). A quantitative estimate for the inhomogeneous strain in each film was obtained from the slope of the increase of the XRD FWHM plotted as a function of diffraction angle (for the three diffraction peaks). The inhomogeneous strain along the (0001) direction was found to increase from 1.2×10^{-3} in the x=0 film, to 2.2×10^{-3} in the x=0.36 film. In the same set of films, the low-temperature CL FWHM was observed to increase from 0.047 eV in the x=0 film, to 0.092 eV in the x=0.36 film. The ratio of the CL FWHM to the (0001) inhomogeneous strain is thus approximately constant for this set of films, and has a numerical value of 40 eV. This ratio agrees with the predicted shift of the band gap with (0001) strain, under conditions of tensile biaxial stress in the [0001] plane, according to a recent study of the electronic deformation potentials of GaN. We plan to examine the correlation between the XRD and CL lineshapes in more detail, to determine whether the deformation potential model can be used to predict the complete luminescence lineshape from the XRD lineshape.

Publications:

L.D. Rotter, M.D. Vaudin, J.E. Bonevich and D.L. Kaiser, "Correlation of the Urbach pseudogap of $(Ba,Sr)_yTiO_{2+y}$ thin films with film composition", submitted to Journal of Applied Physics

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Texture Measurements and Effects

Principal Investigator: Mark D. Vaudin

Technical Objectives:

The objectives of the project are to provide US industry with a fast and accurate method for measuring crystalline texture in thin films. A goal of the work and to develop a technique capable of obtaining accurate texture information from films as thin as 20 nm.

Technical Description:

A number of technologically important materials are deposited as thin films on a variety of substrates. Crystallographic and morphological texture strongly affect the properties of these films. For example: the remanent polarization in ferroelectric films such as $Pb_xZr_{1-x}TiO_3$ is texture dependent, affecting their use in non-volatile memory applications; the stiffness coefficients of copper are anisotropic, so that texture can affect uniformity of film behavior during chemical mechanical polishing (CMP), a processing step used in advanced metallization of microcircuits. One problem has been that accurate texture measurements by x-ray diffraction (XRD) have required specialized equipment not available in most laboratories. For this project it was a requirement that a method be developed use the sort of conventional powder x-ray diffractometer that many laboratories do possess, capable of θ-2θ scans and θ scans. The intensity diffracted by thin films is typically low and thus accurate texture measurements using pole figure techniques are slow and difficult.

The technique we have developed measures preferred crystallographic orientation in thin films (and bulk specimens) by recording two x-ray scans from the sample, 1) a conventional θ-2θ scan of a Bragg peak from the textured planes, and 2) a rocking curve using this peak. The θ scan contains the required texture information but the intensities must be corrected for background, defocussing and absorption to obtain the true texture profile. The Bragg peak scan is used to make the defocussing correction. The absorption calculation requires knowledge of the film thickness and the x-ray absorption coefficient of the material.

Now that the texture of thin films can be quickly and accurately measured, we have started to apply the technique to thin films of $BaTiO_3$ deposited by pulsed laser deposition (PLD). The texture of the films is affected by a large number of factors, including the nature of the substrate, and the film deposition conditions such as substrate temperature, the total energy and energy density of the laser beam, and the ambient environment of the deposition chamber. We have selected the laser energy density (fluence) and the total gas pressure in the chamber as our independent variables. In addition to texture characterization, microstructural characterization by SEM, AFM and TEM are being

carried out to correlate with the XRD texture measurements so that mechanisms and driving forces for texture development can be determined.

External Collaborations:

Tom Shaw and coworkers (IBM, Yorktown Heights) have prepared very thin (~30 nm) barium strontium titanate films on Pt/Si substrates for DRAM applications.

Tom Ritzdorf and coworkers at Semitool Inc. have prepared electroplated Cu films for advanced metallization research.

Cheol Seong Hwang at Seoul National University provided Pt/SiOx/Si substrates designed to have different preferred orientations, which will affect the texture of films grown on the substrates and allow anisotropic properties such as remanent polarization to be optimized. Conventional XRD indicated (100), (110) and (111) textures. The rocking curve technique confirmed fairly strong (110) and (111) texture but showed that the (100) texture was very weak.

Planned Outcomes:

A technique to measure texture, particularly in thin films, will be available that will benefit US industry and academia by allowing fast, accurate texture measurements using conventional powder x-ray diffractometers. The software and documentation will be available on request. The technique will be applied (both at NIST and off-site) to characterize texture and texture evolution in systems where materials properties are strongly influenced by preferred crystallographic orientation, thus allowing rapid specimen evaluation.

Accomplishments:

A software package for Windows 95 has been developed to perform the intensity correction calculations and provide the user with texture data in the form of corrected rocking curves. The package has been distributed to a number of users for field testing purposes.

The film thickness/x-ray absorption correction has been validated. Corrected rocking curves to measure (111) texture have been obtained from a 1.6 μm thick electroplated Cu film (provided by Semitool Inc.) using both the 111 and 222 Bragg peaks. Corrections were applied using a range of film thicknesses and the best fit between the two texture plots occurred for the true film thickness of 1.6 μm.

The background correction developed for weakly textured thin films has been validated. Weak asymmetric 110 texture in bimodally textured $BaTiO_3$ thin films has been measured at two specimen settings related by a 180° rotation about the specimen normal. When the background intensity was measured and subtracted, mirror image rocking curves were obtained.

PLD films of $BaTiO_3$ (BT) on a $Pt/Ti/SiO_2/Si$ substrate showed a bimodal texture by XRD with strong 111 and 110 peaks; the Pt was very strongly (111) textured. TEM observations indicated mechanisms for these textures with epitaxy between the textured Pt and BT producing (111), and multiple twinning of the (111) BT grains leading to (110) oriented BT. These observations differ from previous observations on a substrate that was heat treated in oxygen before deposition where (001) and (111) textures were observed, but no (110).

Publications:

Mark D. Vaudin, Martin W. Rupich, Martha Jowett, G.N. Riley and J. F. Bingert, "A Method for Crystallographic Texture Investigations Using Standard X-ray Equipment," J. Mat. Res., Vol 13, 2910-2919 (1998).

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: Thermal Meaurement Development

Principle Investigators: Albert Feldman, Eduardo J. Gonzalez, Daniel Josell, and Grady White

Technical Objectives:

The objectives of this work are to develop techniques that measure, with small uncertainty, the thermal diffusivity or conductivity of thin films and, subsequently, to transfer the techniques to industry. Included in the idea of technique development are modifications of current models, as needed, and the organization of multi-laboratory experiments to evaluate reproducibility and accuracy of the measurement processes.

Technical Description:

Thermal measurements are currently being made using three a.c. techniques: photo-thermal deflection (PTD), infrared radiometry, and the three-omega (3ω) method. For the first two measurements, an amplitude-modulated Ar^+ laser is focussed onto the specimen surface to provide a periodic heat source. In the PTD measurement, a HeNe probe laser beam is passed through the heated air adjacent to the specimen and the refraction of the probe is measured. In contrast, the infrared radiometry measurement uses an i.r. detector to monitor the heat generated in the film directly. In both experiments, the measured signals are functions of the thermal diffusivity values in the films and the substrate as well as of any thermal resistance at the film/substrate interface. In the 3ω method, a four-probe circuit element, in the shape of a wire, is deposited onto the specimen surface. An a.c. voltage applied to the outer probes at frequency ω provides a modulated resistance-heating source at a frequency of 2ω. The thermal conductivity of the specimen controls the temperature in the deposited probe wire; the wire temperature is inferred through measurements of the wire resistivity.

External Collaborations:

The Ceramics Division is leading an international round robin under the auspices of the Versailles Project on Advanced Materials and Standards (VAMAS). Eighteen laboratories have agreed to participate in order to compare their measurement procedures for measuring the thermal conductivity of a set of thin films prepared at NIST by Don Novotny of the NIST Semiconductor Electronics Division.

Planned Outcomes:

A critical assessment of the ability to measure the thermal conductivity of thin films is an expected outcome of this work and the organized round robin. In particular, physical limitations of both the

PTD and 3ω techniques with regard to measuring thin films as a function of both film and substrate thermal properties will be determined and modeled.

Accomplishments:

PTD of Cu Thin Films: Thermal diffusivity measurements of Cu films on fused-quartz substrates using the PTD have been conducted as a function of film thickness. The thermal diffusivity of Cu films (1.12 $cm^2 \cdot s^{-1}$ at room temperature) was measured with a standard uncertainty of < 10% in films of thickness ranging from 4.75 μm to 70 nm. This work has shown that the PTD technique is capable of providing quantitative characterization of films with thicknesses that are typically encountered in electronic components.

Thermal conductivity round robin: On the basis of a Workshop on Thin Film Thermal Conductivity Measurement held last year at the 13th Symposium on Thermophysical Properties, NIST has organized a round robin for measuring the thermal conductivities of a series of films. The specimens consisted of silicon dioxide films of thickness 50 nm, 100 nm, 200 nm and 500 nm on silicon wafers. The film thicknesses were measured ellipsometrically. The specimens have been distributed to the participants.

The Three Omega Method: The 3ω method has been placed into operation for measuring the thermal conductivity of bulk and thin film materials. The experimental apparatus and the electronic circuits needed for the measurements were constructed. A progammable oven has been installed and interfaced with the computerized data acquisition system for performing measurements between 20 °C and 60 °C. The experimental procedure for calibrating, measuring, and computing the thermal conductivity has been established.

The thermal conductivities of a microscope slide and fused silica slide were measured to evaluate the 3ω procedure. The table compares the measured results (mean value ± standard uncertainty) of the fused silica slide with handbook values for fused silica.

Comparison of the Thermal Conductivity of Fused Silica
obtained by the 3ω Method with the Literature Value

Temperature	Thermal Conductivity ($W \cdot m^{-1}K^{-1}$)	
	measured value	literature value *
20 °C	1.36 ± 0.01	1.37
60 °C	1.46 ± 0.02	1.43

*Thermophysical Properties of Matter, TPRC Data Series, Vol. 2, Thermal Conductivity, Nonmetallic Solids, Y.S. Touloukian, R.W. Powell, C.Y. Ho, and P.G. Klemens (IFI/Plenum, NY, 1970)

Publications:

A. Feldman and N.M. Balzarettia, "A modification of Ångström's method that employs photothermal radiometry to measure thermal diffusivity: application to CVD diamond," Rev. Sci. Instrum. **69**, 237-243 (1998).

A. Feldman, N.M. Balzaretti, A.H. Guenther in *Laser Damage in Optical Materials: 1997*, G.J. Exarhos, A.H. Guenther, "Review of a workshop on Thin Film Thermal Conductivity Measurements," M.R. Kozlowski, and M.J. Soileau, Editors, Proc. SPIE Vol. 3244, pp. 420-433 (1998).

PROGRAM TITLE: Ceramic Thin Film Measurements and Standards

PROJECT TITLE: X-ray Procedures

Principal Investigators: Charles E. Bouldin, James Cline and Bruce D. Ravel

Technical Objective:

The objective of this work is to provide U.S. industry with advanced x-ray characterization methods for evaluating materials used in electronic and photonic applications.

Technical Description:

Most technologically important photonic and electronic materials are prepared as thin films on a variety of substrates. The properties of such films are dependent upon the phase composition, stoichiometry, texture of the phases, strain, and the film thickness. We are developing a variety of x-ray methods to characterize these features of films, including x-ray absorption and resonant x-ray diffraction using synchrotron radiation (National Synchrotron Light Source, Brookhaven National Laboratory), and x-ray reflectivity and diffraction using conventional laboratory x-ray sources and rotating anode sources.

External Collaborations:

Extended x-ray absorption fine structure (EXAFS) spectroscopy has been applied to several thin film systems to determine variations in structure and composition. This work has been done in collaboration with Texas Instruments, Advanced Technology Materials, Inc., North Carolina State University, Argonne National Laboratory, Samsung Electronics, City University of New York, University of Washington and Johns Hopkins University. X-ray reflectivity has been used to measure thicknesses of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) films obtained from IBM.

Planned Outcomes:

The synchrotron x-ray studies will provide insight into the local structural variations in BST films due to small changes in film composition that may be correlated with changes in the dielectric constant. This information is of fundamental importance in understanding the dielectric response of these films, which are being developed by IBM, Motorola, and Micron for use in dynamic random access memory devices. The development of techniques to measure film thickness and interface roughness by x-ray reflectivity and texture by x-ray diffraction would have broad-based applicability to US industries producing thin film devices.

Accomplishments:

A series of slightly Ti-rich BST films on $Pt/SiO_2/Si$ substrates with Ti concentrations in the range 51.0 % to 53.5 % were obtained from Advanced Technology Materials, Inc. The dielectric properties of these 30 nm thick films were characterized by North Carolina State University; the dielectric constant was found to decrease by nearly 50% when the atom fraction of Ti increased from 51.0 % to 53.5 %. We measured these films by several x-ray techniques to look for structural changes that could possibly be correlated with the observed changes in the dielectric properties. Conventional θ-2θ x-ray diffraction measurements demonstrated that the lattice parameter of the BST phase in these films does not change with the Ti content. However, the EXAFS measurements showed significant, systematic changes in several features of the fine structure spectra with changes in the Ti concentration. In the ideal BST structure, the Ti atoms occupy the near-center position in an oxygen octahedron. The measured changes in one feature of the spectra are consistent with a distortion of the oxygen octahedra which increases with increasing atom fraction of Ti. It is possible that the distortion is due to a shift in the Ti atoms from the central position; this will be examined further by x-ray diffraction studies at the Advanced Photon Source at Argonne National Laboratory. This distortion is the same structural change that is associated with the ferroelectric phase transition in $BaTiO_3$ and may account for the observed decrease in the dielectric constant with increasing atom fraction of Ti.

We have initiated x-ray reflectivity measurements of film thickness in a series of BST films on $Pt/SiO_2/Si$ substrates from IBM. Preliminary results suggest that it is possible to determine thickness with a relative standard uncertainty of 0.5%, i.e., about 0.1 nm uncertainty in a 30 nm thick film. These results also suggest that, with further analysis, it may be possible to determine the roughnesses of the surface and buried interfaces from the reflectivity data.

An x-ray diffraction technique has been developed to measure texture in thin film materials using conventional x-ray diffraction equipment; this project entitled "Texture Measurements and Effects" (M. D. Vaudin) is discussed in a separate section of the Ceramic Thin Film Measurements and Standards program.

The design of a high resolution, thin film diffractometer has been finalized, and the components are being fabricated and assembled. This unique instrument will provide the following capabilities: metrologically credible d-spacing measurements; macro-strain measurements; micro-strain and particle size/shape determinations; full texture and epitaxy determinations; and x-ray reflectometry. The hardware includes a rotating anode source, focusing parabolic mirrors and monochromator crystals for incident beam preparation, optically encoded theta and two-theta goniometers, a Eulerian cradle for phi and chi sample rotation axes, and an optical bench. The features will include the following: an x-ray source with ten times the intensity of conventional sources; a large area, parallel, monochromatic incident beam; ultra high accuracy in theta and two-theta measurements; full sample orientation capability; use of modular components; and a layout that allows for flexibility with regard to future expansion in capabilities. The instrument, scheduled to be operational in Spring 1999, will be used for a variety of film measurements, including the texture and x-ray reflectivity studies

discussed here, as well as for the "X-ray Standards" project discussed in a separate section of this report.

Publications:

J.C. Woicik, J.O. Cross, C.E. Bouldin, B. Ravel, J.G. Pellegrino, B. Steiner, S.G. Bompadre, L.B. Sorensen, K.E. Miyano, J.P. Kirkland, "Diffraction anomalous fine structure study of strained Ga(1-x)In(x)As on GaAs(001)," Phys. Rev. B, Vol 70, R4215, (1998).

J. O. Cross, M. Newville, J. J. Rehr, L. B. Sorensen, C. E. Bouldin, G. Watson, T. Gouder and G. H. Lander, M. I. Bell, "Inclusion of local structure effects in theoretical x-ray resonant scattering amplitudes using ab initio x-ray-absorption spectra calculations," Phys. Rev. B., Volume 58, 11215 (1998).

B. Ravell, C.E. Bouldin, H. Renevier, J.L. Hodeau and J.F. Berar "Edge Separation Using DAFS," ESRF-Newsletter No. 31 (Sept. 1998).

DENTAL AND MEDICAL MATERIALS

The Dental and Medical Materials Program provides basic materials science, engineering, test methods, and standards to sectors of the health care industry for the development of new or improved materials and delivery systems. This program focuses on (1) development of improved dental restorative materials with greater durability, wear resistance and clinical acceptability; (2) development of improved bone fixation materials and (3) evaluation of biomaterials.

Dental restorative composites are heterogeneous materials having three essential phases: (1) a polymeric matrix which comprises the continuous phase, (2) fillers of various types, sizes, shapes and morphologies which constitute the disperse phase and (3) an interfacial phase that, in varying degree, bonds the continuous and disperse phases into a unitary material rather than a simple admixture. While all three phases are important in determining the properties of the composites, this program is focused primarily on the interfacial and polymer matrix phases. Since the polymerization shrinkage that occurs in the matrix phase is one of the most commonly cited deficiencies of dental restorative composites, resources are allocated to develop high conversion, durable, low shrinkage polymeric materials for use in dental resin and composite applications. The polymeric matrix of a dental composite typically is formed by free radical polymerization of a resin which is one or more vinyl monomers, usually of the methacrylate class. Polymerization is started either by the formation of initiating radicals from chemical reduction-oxidation (redox) reactions or by photochemical redox reactions.

Although only a minor component of these composites, the interfacial phase that develops from the interaction of the silane coupling agent with the polymer matrix and the siliceous filler exerts a profound effect on the properties of the composites. Because these composites are used in an aggressive, aqueous environment that constantly challenges the vulnerable silane mediated polymer-filler bond, understanding of this critical interfacial phase is being acquired so that strategies can be developed for its improvement.

The occupational and environmental hazards associated with the use of mercury-containing dental alloys are a recurring source of public concern. Since dental amalgams have performed exceedingly well over more than one hundred years, the development of a direct filling material still based on the common constituents of dental amalgams, other than mercury, is desirable. This project is focused on acid-assisted consolidation of chemically precipitated silver powders and property measurements of hand consolidated test compacts prepared with the tools and procedures normally employed by dentists. The observed values of flexural strength for the silver compacts were equal or superior to mercury amalgams. Corrosion resistance, microleakage and marginal toughness values of the compacts were found to be superior to those of amalgams. Wear and biocompatibility studies on the hand consolidated compacts are in progress.

Besides the dental materials projects, efforts are directed toward the development of improved bone fixation materials and the evaluation of biomaterials. A project, carried out in collaboration with the American Dental Association and the National Institute of Dental Research, is directed at enhancing

the biocompatibility and mechanical properties of composite bone cements. The biomaterials evaluation effort centers on the NIST Orthopedic Wear Consortium which consists of four companies to develop accelerated wear test procedures for rapid screening of materials used in hip and knee replacements. This will accelerate the introduction of new biomaterials into practice.

Dental and medical research directions in support of the goals are established in collaboration with the American Dental Association (ADA), the National Institute of Dental Research, the National Heart, Lung and Blood Institute, the US Food and Drug Administration, and guest scientists from the U.S. Navy and the U.S. Public Health Service. NIST has hosted research associates from ADA since 1928. Currently, the ADA Health Foundation sponsors 30 research associates at NIST. The collaborative relationship between that professional association and the federal government is unique, and continues to develop and transfer important new technologies to dentistry and medicine.

PROGRAM TITLE: Dental and Medical Materials

PROJECT TITLE: Accelerated Wear Test Development for Biomaterials

Principal Investigator: Stephen M. Hsu

Technical Objective:

The obective of this project is to develop an accelerated test method to effectively evaluate biomaterials used in total joint replacement.

Technical Description:

The approval process for materials used in human joints is expensive and time consuming. As new materials become available, a rapid screening methodology is needed to shorten the product development cycle, improve product reliability, and develop more durable components for the total joint replacements. The consortium was formed in October 1996, by NIST and six orthopaedic companies for a duration of two years. A technology survey conducted among the six companies to assess the current state-of-the-art in biomaterials evaluation indicated that a new wear tester capable of cross-shear and computer controlled program-loading was needed. These features would accelerate the test without changing the basic mechanisms of human joint movements. Since there was no equipment available to conduct such tests, the design and construction of the new wear tester and the development of the test method to discriminate three known materials was initiated. In this effort, wear test development is pursued at NIST, and the orthopedic consortium members supply hip and knee joint replacement parts. The materials currently being studied are ultrahigh molecular weight polyethylene (UHMW/PE) and cobalt-chromium alloys.

Collaborations:

The consortium was formed in October 1996, by NIST and six orthopaedic companies for a duration of two years. The NIST contribution is a joint project between the Polymer Division and the Ceramics Division. Dr. John Tesk serves as the project manager providing liaison between NIST and the consortium members as well as participating in the technical effort. Dr. Dan Fischer (NIST) and Dr. S. Sambasivan (Guest Scientist, NSLS) of the Materials Microstructural Characterization Group in the Ceramics Division participated in the analysis using x-ray absorption techniques. The consortium members provide guidance, materials, and data to the project as well as support for Dr. Ming Shen from University of Maryland to work on the project. Prof. Aris Christou from University of Maryland also provides support and guidance to the project.

Planned Outcomes:

The anticipated outcomes are: 1) the design of a novel wear tester that can be computer controlled to mimic human joint loading characteristics; 2) the development of an accelerated test procedure that can effectively evaluate biomaterials for joint replacement.

The field of biomaterials has become a rapidly growing business throughout the world. These new materials offer a great opportunity for technological advances. However, the cost of qualifying a biomaterial in the US is high as well as time consuming. A rapid, effective screening test method will reduce costs, cut the lead time, and help to maintain the competitive edge of the U.S. biomaterials industry.

Accomplishments:

A novel wear tester was successfully designed and built. The tester has cross-shear motion provided by two independent motor-driven stages containing the test specimens. By varying the frequency and stroke length of the two stages, a wide variety of cross-shear patterns can be generated. A computer controlled spike loading capability was implemented. Based on this tester, a short-duration test method was developed that mimics the loading history of human joints. Test results on three UHMWPE materials with known wear levels supplied by the Orthopaedic Consortium suggest that the correct ranking of materials was achieved within a week of testing. As a result of this development, the consortium agreed to continue the collaboration for another two years (to October 2000) to provide scientific understanding of the mechanismsin short-term testing so that long-term performance can be simulated more effectively by the test.

Publications:

M. C. Shen, S. M. Hsu, J. Tesk, and A. Christou, A Novel Multiaxial Wear Tester for Accelerated Testing of Materials," accepted for publication in Orthopaedic Research Society.

D.A. Fischer, S. Sambasivan, M. C. Shen, and S. M. Hsu, "Wear Induced Molecular Orientation in UHMWPE Measured by Soft X-ray Absorption," submitted to Biomaterials Research Society.

S. Sambasivan, D. A. Fischer, M. C. Shen, and S. M. Hsu, "Effects of Wear Motion on UHMWPE Molecular Orientation," submitted to Biomaterials Research Society.

H. W. Fang, M. C. Shen, U. Cho, J. Tesk, and A. Christou, S. M. Hsu, "Generation of Different UHMWPE Particle shape by Wear through Surface Texturing," submitted to Biomaterials Research Society.

"Amorphous Alloys Containing Cobalt for Orthopaedic Applications," J. Tesk, C. E. Johnson, D. Skrtic, M. S. Tung, S. M. Hsu, Proceedings of ASTM Special Symposium 'Cobalt-based alloys for Biomedical Applications, ASTM STP 1365, 1998.

MAGNETIC MATERIALS

Magnetic materials are pervasive throughout our society. They are used, for instance, in magnetic recording media and devices, in all motors, in all transformers, on credit cards, as permanent magnets, as magnetic sensors, on checks, in theft control devices, in automotive and small engine timing devices, in xerographic copiers, in magnetic resonance imaging (MRI) machines, in microwave communications, in magnetic separation, and in magnetic cooling. Magnetic materials include metals, ceramics and polymers at different size scales ranging from large castings to particulates, thin films, multilayers and nanocomposites.

In the present trend to make devices smaller, thereby reducing weight or increasing storage density, new magnetic materials are constantly being developed. One critical need for implementation of these materials is the development of the measurement science needed for their characterization, in terms of both material properties and performance. This is the focus of the Magnetic Materials Program. Proper measurements of key magnetic properties, determination of the fundamental science behind the magnetic behavior of these new materials, analyses of the durability and performance of magnetic devices and development of Standard Reference Materials are key elements of this program. Some information is only obtainable by the use of unique measurement tools at NIST like the neutron diffraction facilities at NCNR, or the magneto-optic indicator film apparatus for observation of magnetic domain motion. Of particular interest is understanding the magnetic behavior of low dimensional systems, in which one or more characteristic dimensions have been reduced to nanometer sizes. For these new materials, however, it is not known whether their exciting novel behavior is due to new physics or to a logical extension of large-size behavior to small dimensions. Consequently, implementation of this new type of material into marketable products is significantly delayed. NIST is providing the measurement science to address this critical unknown.

Areas of present study include the following:

- processing of magnetic multilayers for optimal giant magnetoresistance effect
- observation and micromagnetic modeling of magnetic domains for understanding magnetization statics and dynamics in advanced and conventional materials
- measurement and characterization of nanoscale magnetic interactions in multilayers, nanocomposites, and low-dimensional systems, needed for understanding and applying the physics of these materials
- measurement and modeling of the enhanced magnetocaloric effect in nanocomposites
- structure and magnetic characterization of new superconducting materials

- nanotribology of magnetic hard disks, measurement of stiction, friction, and wear at the nanometer scale

- measurement and understanding the origin of magnetic exchange bias in conventional and advanced magnetic structures and devices

- development of magnetic sensors of mechanical properties for incorporation as *in situ* controls in a steel mill

- development of a measurement system for the preparation of an absolute magnetic moment standard

By experimentally addressing important issues in magnetism, by bringing together the industrial and scientific communities through the organization of workshops and conferences in the area, and by the development and preparation of appropriate standards, NIST acts to accelerate the utilization of advanced magnetic materials by the industrial sector, and to enable industry to take advantage of new discoveries and innovations. In addition, close linkage with the national storage industry consortium (NSIC) which consists of 38 companies and a score of universities allows industrial relevance and partnership. Additional collaborations with Xerox, General Motors, Hewlett Packard, IBM, Seagate, and Motorola Corporations, for example, enable NIST to leverage its activities with the much larger, but complementary, capabilities of other organizations.

PROGRAM TITLE: Magnetic Materials

PROJECT TITLE: Nano-Tribology

Principal Investigators: Stephen M. Hsu, Richard S. Gates, Patricia A. McGuiggan, and Daniel A. Fischer

Technical Objective:

The objective of this project is the development of measurements of friction, wear, and durability of magnetic hard disk systems and the measurement of the mechanical and tribological properties of the ultra-thin lubricating film on the disks. Measurement and characterization of such thin films will enable the development of future ultra-high density data storage technology.

Technical Description:

The development of ultra-high density magnetic hard disk technology requires nanometer scale measurements of friction, wear, and durability between the head and the disk. Current technology with an areal binary bit density of 8 μm^{-2} (2 Gbit/in^2) uses an air bearing design flying at 20 nm above the disk. At 160 μm^{-2} (40 Gbit/in^2) areal density, the head needs to fly at 5 nm above the disk. Computational models suggest that ultimate density of 400 μm^{-2} (100 Gbit/in^2) may be possible. Sufficient protection of the disk surface against friction and wear of the thin carbon overcoat, (which in combination with the lubricant layer is 1 nm thick) is the critical technological barrier as the distance between the head and disk becomes smaller. Measurement techniques probing progressively smaller scales must be developed to study these systems. These measurements are difficult to conduct and the phenomena are difficult to analyze because of the small size scale.

Working in conjunction with the National Storage Industry Consortium (NSIC) Tribology Working Group, we are developing new and novel concepts in protecting the magnetic hard disk surface *via* organized molecular film structures. Various monomolecular films are deposited on ultra-smooth disks over different carbon overcoat materials. Some of the disks are evaluated by industrial collaborators using component testing. Some of the disks are evaluated using the unique facilities at NIST. Surface characterization techniques are being developed to measure molecular orientation, film thickness, and surface bonding strengths. Fundamental measurements of surface forces, film strength, and nano-mechanical properties are also being studied to support the technological development effort by U.S. industries.

Collaborations:

Part of the project is supported by intramural funding from the NIST Advanced Technology Program (ATP) in support of NSIC projects. NSIC consists of over 30 companies and some 25 universities. We work closely with the Tribology Working Group which consists of IBM, Readrite, Komeg, Seagate, University of California at Berkeley, University of California at San Diego, Northwestern

University, and Carnegie Mellon University. We also work with the University of Texas at Houston, University of North Carolina, and industrial suppliers of chemicals.

Planned Outcomes:

In conjunction with NSIC, this project will: (1) develop laboratory test procedures to evaluate the wear and lubrication characteristics of magnetic hard disk systems, (2) establish a model of how monomolecular films interact and protect the magnetic disks, and (3) determine relationships between thin film structures and their nano-mechanical properties.

Accomplishments:

Various organic monolayers and monomolecular films were designed and deposited on the magnetic hard disks (CH_x and CN_x coated surfaces). The coated disks were evaluated for friction and durability in studies by the University of California at Berkeley, using constant start and stop tests (CSS), and at NIST, using the high speed spin stand inclined plane tests. Films that had strong adhesion and cohesion characteristics performed much better. A series of molecules that had different substitutions of fluorine atoms and hydrogen atoms were evaluated. Molecules with the same structures but with fluorine atoms performed better than the hydrogen substituted molecules. Supercritically separated perfluoroalkylether fractions were obtained from our industrial collaborators and tested. There was a critical molecular weight (or a critical chain length) that was needed to protect the hard disk surface.

Lateral force measurements using the atomic force microscope (AFM) and the surface forces apparatus (SFA) were compared. Two different probes were used in the AFM measurements; a sharp silicon nitride tip (radius $R \approx 20$ nm) and a glass ball ($R \approx 15$ μm). The lateral force was measured between the (silicon nitride or glass) probe and a mica surface which had been coated by a thin lubricant film. In the SFA, a thin lubricant film separated two molecularly smooth mica surfaces ($R \approx$ 1 cm) which were slid relative to each other. Perfluoropolyether (PFPE) and polydimethylsiloxane (PDMS) were used as the lubricant films. With a large probe, the PFPE film showed much lower friction than PDMS. However, as the size of the probe decreased, the difference in the measured friction decreased until no clear distinction between the tribological properties of the films could be made.

Carbon overcoats are used on the magnetic hard disk surface to minimize friction and wear of the magnetic surface. The friction of amorphous carbon surfaces was measured in the surface forces apparatus. This apparatus can not only measure the friction and applied load, but the microscopic area of contact as well. The results show that friction of the amorphous surfaces is adhesion controlled (dependent upon the area of contact). The friction was also found to decrease with increasing humidity.

Vapor phase deposition of thin films on hard disks was also studied to support an ATP project. A vapor phase deposition apparatus was designed and contracted to Carnegie Mellon University to build. The apparatus is scheduled to be ready in January, 1999.

Characterization of lubricant thin films was also carried out at Brookhaven National Laboratory using the ultrasoft x-ray beam line. X-ray near edge absorption spectroscopy can be used to determine molecular orientations, monomolecular film thickness, and the nature of the chemical bonding between the molecules and the carbon overcoats. Samples were obtained from IBM and Dow Chemical Co. to study the interactions of perfluoroalkyl ethers and phosphazene on different carbon overcoated hard disks. Results showed that Ar sputtered carbon overcoat interacted strongly with the phosphazene molecules, while the hydrogenated carbon (the current hard disk coating) did not. This interaction explains why the phosphazene molecules tended to segregate from the perfluoroalkyl ethers on the hard disk and the preferentially adsorbed onto the head surface, thereby reducing the catalytic decomposition of the alumina on the perfluoroalkyl ethers.

Publications:

B. M. DeKoven, D. A. Fischer, G. E. Potter, D. J. Perettie, S. Bhatia, T. A. Morgan, and S. M. Hsu, "Chemistry/Orientation of Lubricants on Hard Disk Magnetic Media Substrates Using Near Edge X-ray Absorption Fine Structure," submitted to the J. of Vacuum Science and Technology A.

Y. Wang and S. M. Hsu, "Lubricated Friction and Wear Simulation of Multi-scratches in Asperity-asperity contact," *Wear* **217**, 104-109 (1998).

P. M. McGuiggan, J. Zhang, and S. M. Hsu, "Comparison of Friction Measurements Using Atomic Force Microscope and the Surface Forces Apparatus: the issue of scale," submitted to Tribology Letters.

D. J. Perettie, B. M. DeKoven, T. A. Morgan, D. A. Fischer, S. M. Hsu, F. E. Talke, H. J. Kang, and C. S. Bhatia, "The Use of Advanced Lubricant Additives to Enhance the Performance of the Head/Disk Interface: The Effects of Surface Energy and Orientation," accepted for publication in STLE

MECHANICAL PROPERTIES OF BRITTLE MATERIALS

Mechanical properties are the source of the greatest benefits as well as the most severe limitations of ceramic materials. Owing to their high strength-to-weight ratio, their relatively inert behavior in aggressive environments, their high hardness and wear resistance, and their ability to withstand significantly higher temperatures than metals or polymers, ceramic materials offer the potential for major improvements in component design for a wide range of applications. On the debit side, however, ceramics typically exhibit statistically variable brittle fracture, environmentally enhanced subcritical crack growth, sensitivity to machining damage, and creep-deformation behavior at elevated temperatures. Additionally, a lack of techniques for detecting and quantifying critical flaws before failure ensues, severely curtails current uses of ceramics. Unpredictable failure behavior of ceramics stems from three sources: (1) limited data and a deficiency of basic understanding of failure processes in ceramics; (2) limited standard test techniques to permit inter-laboratory comparisons of materials behavior and collection of engineering data; and (3) inadequate models and statistical techniques for life prediction and reliability analyses. The Mechanical Properties of Brittle Materials Program has components specifically addressing each of these issues.

Basic understanding of mechanical behavior of ceramics is investigated both at room temperature and at elevated temperatures. At room temperature, mechanical properties and failure processes are investigated in polycrystalline ceramics, glasses, and ceramic matrix composites as a function of microstructure, environment, and processing conditions. Material systems include glasses for spacecraft windows, thermal barrier coatings, and aluminum nitride substrates. Microstructural stresses related to enhanced fracture toughness and damage mechanisms are measured via micro-Raman techniques in heterogeneous microstructures and correlated with micro-mechanical modeling. Micro-mechanical computer simulations are used to elucidate distributions of residual stresses and microcrack damage in highly anisotropic ceramics as a function of crystallographic texture. At elevated temperatures, the basic mechanisms responsible for crack growth, creep, and creep-rupture are investigated for various silicon nitride compositions, and for membrane and fuel cell materials.

To improve interlaboratory comparisons and to increase confidence in generated data, new standard test techniques for hardness, strength, and toughness are being developed and tested in round-robin experiments. Research and interlaboratory studies in instrumented indentation address the use of this technique for measuring elasticity and hardness of thin films and coatings. Micro-Raman techniques are being developed and calibrated so that quantitative assessments of microstructural residual stresses can be mapped for heterogeneous microstructures. At elevated temperatures, new creep specimens are designed which permit higher stresses with reduced non-gage section failures. Intra- and inter-laboratory studies demonstrated the robustness of these geometries. International inter-laboratory studies are underway to elucidate their relationship to alternate testing geometries.

Finally, techniques to predict lifetimes of ceramic materials and glasses under constant and variable loading conditions are being developed. A nonparametric bootstrap approach for assessing the

confidence of lifetime predictions is investigated and compared with analytical techniques. Work includes applying these techniques to aluminum nitride materials for thermal management systems and to fused silica and other glasses for spacecraft window applications. A new experimental procedure is being explored for characterizing time-dependent failure under static loads.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Design of Space Shuttle Windows

Principal Investigators: Linda M. Braun, Jay S. Wallace, and Edwin R. Fuller, Jr.

Technical Objective:

The objective of this project is to assist NASA through the development of measurement and analytical procedures, using a fracture mechanics based methodology, for determining mechanical reliability and for calculating projected lifetime of space application materials.

Technical Description:

This project involves measurement of mechanical properties, and development of analytical techniques, that are required to determine mechanical reliability and to calculate the projected lifetime of brittle materials. Two different types of glass specimens are being investigated. The first consists of two grades of fused silica used for space shuttle windows, and the second was a sodium aluminosilicate glass with and without a chemical temper for use in the International Space Station. The thin, chemically tempered layer is used to strengthen the glass by putting the surface of the material in compression.

The mechanical properties that are being measured include critical stress intensity and subcritical crack growth parameters from applied moment double cantilever beam (AMDCB) specimens, static fatigue and dynamic fatigue *via* ring-on-ring biaxial flexure testing and *in situ* observations of crack propagation to failure. Dynamic and static fatigue tests are used to verify the validity of the crack growth parameters determined from large cracks using AMDCB tests for small intrinsic defects.

External Collaborations:

This research is being conducted in collaboration with NASA, Boeing, and Corning, Inc.

Planned Outcomes:

The results from these experiments are used to qualify (certify) both the fused silica and aluminosilicate glass for space applications.

Accomplishments:

A comparison of the crack growth behavior of the two grades of fused silica manufactured by Corning, Inc. was performed. Applied moment double cantilever beam critical stress intensity results from both grades of fused silica material are identical within the statistical error of the measurement technique (≈ 0.72 MPa $m^{1/2}$). In addition, N values determined from the AMDCB crack growth data,

assuming power law crack growth, for both grades of fused silica are identical within the statistical error of the measurement technique (N≈38). Both the K_{IC} and N values measured in this study are in excellent agreement with published literature values. No fatigue limit or corrosion limit was observed for either material. Comparison of the N values determined from dynamic and static fatigue measurements indicate that there is no significant difference in the values obtained from these short crack tests and those values obtained from long crack AMDCB tests. It appears that any differences can be explained by the sampling statistics of the fatigue tests.

The average value for critical stress intensity determined from the AMDCB for the sodium aluminosilicate glass is 0.726 $MPa \cdot m^{1/2}$ with a standard uncertainty of 0.014. The N value determined from the AMDCB crack growth data, assuming power law crack growth, is 23.7. The fitting parameters assuming an exponential law are $V_0 = 10^{-15.9}$ and b = 24. A fatigue limit or stress corrosion limit was observed for this material. A stress corrosion limit is an important engineering parameter since it allows one to calculate the applied stress below which the material exhibits no delayed failure. Comparison of the N' value determined from dynamic fatigue measurements on indented samples with the N value determined from AMDCB, indicate that there is no significant difference in the values obtained from short crack tests and those values obtained from long crack AMDCB tests.

Publications:

L.M. Braun, J. Wallace, and Edwin R. Fuller, Jr., "Fracture Mechanics and Mechanical Reliability Study: Comparison of Corning Code 7980 and Code 7940 Fused Silica," submitted NIST Internal Report

L.M. Braun, J. Wallace, and Edwin R. Fuller, Jr., "Fracture Mechanics and Mechanical Reliability Study of Chemcor Glass," submitted NIST Internal Report

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: High Temperature Creep and Reliability

Principal Investigators: William E. Luecke and Sheldon M. Wiederhorn (MSEL)

Technical Objectives:

The principal objectives of this project are to develop creep test methodology and to study the creep characteristics of brittle materials at high temperature. This research is designed to assist industry in the evaluation, design, and development of advanced structural ceramics for use as high temperature components in land-based heat engines for power generation and vehicles, and in the development of measurement methodologies for the evaluation of the necessary high temperature mechanical properties.

Technical Description:

We are studying the mechanisms and statistics of high temperature creep and rupture in advanced ceramics and developing and refining the test methods for these measurements. Using our extensive creep facilities (9 tensile, 3 compression, and 6 flexure machines) we can generate the quantity of data necessary to make databases that allow statistical interpretation of the data. In addition, we can accommodate visiting scientists from industry and academia both to educate them on the use of our techniques as well as conduct tests on experimental grades of structural materials. Further developments and assessments of creep test methods are being pursued by means of an international round robin on tensile creep.

External Collaborations:

Collaborators in this work include David Wilkinson, McMaster University (stress induced grain boundary film redistribution in silicon nitride), Wolfgang Braue, German Aerospace Research Establishment (creep of yttrium silicates), Prof. Georg Grathwohl, Technical University of Bremen (aligment effects on measured tensile creep properties in silicon nitride), Prof. Nitin Padture; University of Connecticut (high temperature slow crack growth in *in situ* toughened SiC), Prof. Jürgen Rödel Technical University of Darmstadt (creep of Al_2O_3-Ni_3Al composites)

Planned Outcomes:

The international creep round robin will establish a precision and bias statement for the ASTM standard for creep testing of ceramics.

A new pure shear creep specimen will enable tests that will be developed and used to distinguish between two alternative models for creep of silicon nitride.

Accomplishments:

Of the 17 laboratories invited to participate, 14 took part in the tensile creep round robin. Currently we are preparing a report to the participants. The range in both time and strain to failure (the ratio, largest value/smallest value ~ 5) is larger than initially expected and will undoubtedly surprise some participants. Our study on alignment effects on measured tensile creep properties of silicon nitride, conducted with Daniel Grimme (Tech. U. Bremen, Germany) showed that the measured creep rupture properties of silicon nitride are not significantly affected by misalignment. We constructed a controlled atmosphere furnace for conducting tensile creep of silicon nitride, which should allow us to understand the role of oxidation in high temperature failure mechanisms of silicon nitride.

Publications:

Ralph F. Krause, Jr, William E. Luecke, Sheldon M. Wiederhorn, Jonathan D. French, and Bernard J. Hockey, "Tensile Creep and Rupture of Silicon Nitride," *J. Am Ceram. Soc.* (1998), in press.

William E. Luecke and Sheldon M. Wiederhorn, "A New Model for Creep of Silicon Nitride," *J. Am Ceram. Soc.*, accepted for publication (1998).

S. M. Wiederhorn, W. E. Luecke, and R. F. Krause, Jr., "A Strain-Based Methodology for High Temperature Lifetime Prediction," in press, *Ceramic Engineering and Science Proceedings,* (1998)

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Mechanical Property Modeling

Principal Investigators: Andrew R. Roosen, W. Craig Carter, Stephen A. Langer [Mathematical and Computational Sciences Division (891), ITL], and Edwin R. Fuller, Jr.

Technical Objectives:

This research is designed to assist industry through the development of new paradigms for elucidating micro-physical behavior of real and simulated material microstructures. Theoretical and computational methods are applied to bitmap images to investigate microstructural stresses and strains, fracture, deformation and damage behavior, and other nonlinear phenomena in polycrystalline and multi-phase ceramics and ceramic composites. A particular objective is the creation of tools for the prediction and computation of behaviors in real microstructures with the aim of identification of microstructural features which optimize macroscopic properties in commercial materials.

Technical Description:

Real materials have complex microstructures which can contain distributed second phases, each having its own localized constitutive behavior. Microstructures can also contain cracks, pores, and other features which severely affect performance. A general software tool, called ***OOF*** (for **O**bject **O**riented **F**inite Elements) is being developed which incorporates all such complexity and which organizes local constitutive behavior so that calculations can be performed in systems which would otherwise be intractable. The model incorporates the mechanics and physics of heterogeneous microstructures at the mesoscopic level.

External Collaborations:

This research involves numerous external collaborations including informal joint projects with Donald M. Baskin, Prof. Vinayak P. Dravid, Michael H. Zimmerman, and Prof. Katherine T. Faber, (Northwestern University), Jill Glass (Sandia National Laboratory), André Zimmermann and Prof. Jürgen Rödel (Technische Hochschule Darmstadt), Stefan Lampenecherf and Prof. Wolfgang Pompe (Technische University Dresden), Prof. Anil Saigal (Tufts University), and Chun-Hway Hsueh and Paul Becher (Oak Ridge National Laboratory).

Additionally, more than one hundred researchers have down-loaded the ***OOF*** software from the CTCMS (Center for Theoretical and Computational Materials Science) Software archives, and many of the users have provided us feedback. The ***OOF*** mailing list has over 80 subscribers.

Planned Outcomes:

The ***OOF*** software will be provided to the public in various stages of its development to aid in the development and prediction of commercial materials through virtual materials testing.

Accomplishments:

Version 1.0 of ***OOF*** was released. ***OOF*** has a graphical interface and performs several tasks:

- combines microstructural image data with materials data and constitutive behavior;
- applies (virtual) experimental boundary conditions and/or stress-free localized strains;
- solves for thermoelastic stresses and strain fields;
- predicts and incorporates materials damage; and
- quantifies and visualizes results.

OOF uses image data from real or simulated materials to create a finite element mesh. The program includes tools for selecting and manipulating features in an image, a finite element mesher and solver, and an extensive interface.

A description of ***OOF***, links to the first publicly released version of the program (which may be downloaded as public domain software), an interactive manual, and a "Picture and Simulation Gallery" are available on the internet at URL address:

http://www.ctcms.nist.gov/~wcraig/oof/

Thus far, more than 100 copies of the program have been downloaded.

Publications:

The OOF Manual: Version 1.0, NISTIR 6256, and on-line at URL address:
http://www.ctcms.nist.gov/~langer/oof/Manual/Manual.html

Anil Saigal, E. R. Fuller, Jr., A. A. Langer, W. C. Carter, M. H. Zimmerman, and K. T. Faber, "Effect of Interface Properties on Microcracking of Iron Titanate," *Scripta Met.*, 38, 1449 (1998).

C.H. Hseuh, P.F. Becher, E.R. Fuller, S.A. Langer, and W.C. Carter, "Analytical and Numerical Analyses for Two-Dimensional Stress Transfer", submitted to *Acta Materialia*.

C.H. Hsueh, P.F. Becher, E.R. Fuller, Jr, S.A. Langer, W.C. Carter, "Surface-Roughness Induced Residual Stresses in Thermal Barrier Coatings: Computer Simulations", submitted to proceedings of the 5th International Symposium of Functionally Graded Materials, FGM'98.

C. H. Hsueh, J. A. Haynes, M. J. Lance, P. F. Becher, M. K. Ferber, E. R. Fuller, Jr., S. A. Langer, W. C. Carter, and W. R. Cannon, "Effects of Bond Coat Surface-Roughness on Residual Stresses of Thermal Barrier Coating Systems," submitted to J. Am. Ceram. Soc.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Mechanical Test Development

Principal Investigator: George D. Quinn

Technical Objectives:

Procedures are developed for characterizing ceramics, and standard test methods are prepared for ASTM and ISO consideration. Our goal is to develop procedures that are as technically rigorous as possible while remaining practical and usable by industry.

Technical Description:

Mechanical testing methods for ceramics are created, improved, refined, and standardized. Testing is conducted to gain first-hand experience with a method. Upon reaching a mature prestandardization level, a method is evaluated by round robin(s) which verify the suitability of the method and generate precision and bias data. Foundation work for standard reference materials is performed. Current work is targeted towards fracture toughness, hardness, diametral compression strength, and flexure strength (cylindrical specimens) tests.

External Collaborations:

Industry is consulted for test method standardization needs. The Department of Energy, Office of Heavy Vehicle Technologies, provides programmatic support for some portions of this project. ASTM Committees such as C-28, Advanced Ceramics, E-28 Mechanical Testing, E-08 Fracture and Fatigue, and F-04 Surgical and Medical Devices are consulted and used as forums for creating standards. International collaborations are maintained through the VAMAS program and other fora. International standardization is pursued through ISO Technical Committee 206, Fine Ceramics and contacts in CEN Technical Committee TC 184, Advanced Technical Ceramics.

Planned Outcomes:

Standard practices, test methods, and suitable reference materials will be developed, as appropriate, to establish accurate and reproducible measurements of mechanical properties. Current plans include the refinement of ASTM provisional standards PS 070-97 for fracture toughness, the development of a standard method for the diametral compression strength measurement, and the establishment of ISO standards for flexural strength, hardness, and fracture toughness.

Accomplishments:

ASTM Elastic Moduli Standards
Two new standard methods for elastic moduli determination, E 1875 and E 1876, were adopted by ASTM in Committee E-28, Mechanical Testing. They are clones of the C-28 Advanced Ceramic standards C 1198 and C 1259.

ASTM Fracture Toughness Standard
Intensive work continued to refine the ASTM provisional standard PS 070-97 for fracture toughness. This work was done in cooperation with Prof. I. Bar-On of Worcester Polytechnic, Prof. M. Jenkins of the University of Washington, and Dr. J. Salem of NASA-Lewis. This document is being converted to a full- consensus standard. As an example of our refinement work at NIST, there was some doubt whether the really small single-edge precracked beam (SEPB) specimens in our standard could be tested reliably under 3-point loading. A series of experiments with different fixtures were performed using our reference material specimens (described below). Results were very consistent (within 1% on average) whether we used 3-point, 16 mm span; 4-point 10 mm x 20 mm spans; or 4-point, 20 mm x 40 mm spans, but the short span 3-point rejection rate was appreciably greater. Cracks tended to curve more due to the slight misalignments in the crack tip with the middle roller.

The surface crack in flexure (SCF) method, one of the three adopted in PS-070, was also refined. Dye penetrants were used to make precracks easier to detect. In summary, fluorescent penetrants worked best with coarse-grained materials and less well with fine-grained materials. Finally, we furnished some silicon nitride specimens to NASA-Lewis for Chevron Notch (CN) testing, also one of the three methods in the ASTM standard. As a result of their work, NASA decided to change the CN equations used in PS070 to calculate K_{Ic}. This dramatic change is an important improvement to the ASTM standard and a direct consequence of our SRM work described below. We now have a material for which K_{Ic} is known with a standard uncertainty less than in 1%!

Fracture Toughness Standard Reference Material
Much of our work this year focused on the preparation of a Standard Reference Material (SRM 2100) with certified fracture toughness values. From six billets of hot-pressed silicon nitride, grade NC 132, nearly 1000 specimens were prepared and almost 200 were tested by SCF, SEPB and CN (courtesy of NASA-Lewis). Of the six billets, one was rejected due to a material susceptibility to slow crack growth, and two others due to microstructural inhomogeneities. Approximately 550 specimens from the 3 good billets will be sold in SRM kits of 5 specimens each.

ISO Technical Committee TC 206, Fine Ceramics
Work in this project contributed to five Working Groups (WG) in this ISO TC, WG 2 (Flexural Strength), WG 3 (Hardness),WG 7 (Fracture Toughness by SEPB), WG 8 (Flexure Strength at Elevated Temperatures), and a new WG (Fracture Toughness by SCF). A "Draft International Standard" is being balloted in WG 2. In addition, Mr. Quinn represented the United States in nine WG meetings at the TC 206 meeting in Kyongju, Korea in September, 1998.

VAMAS Technical Working Area 3, Ceramics Projects

Mr. Quinn is the chairman of TWA #3. Meetings were held in Florence, Italy in connection with the CIMTEC conference, in Kyongju, Korea in connection with PACRIM3, and in London with the VAMAS Steering Committee. TWA 3 finished three round robins this year and a fourth is nearing completion:

Conventional Hardness of Ceramic Composites, organized by NIRIN - Sakaguchi / JFCC - Mizuno in Japan. NIST joined as a participating lab and G. Quinn statistically analyzed the results. A VAMAS final report was written. This exercise proved that conventional methods may be applied successfully to whisker-reinforced composites.

Recording (Instrumented) Hardness, organized by BAM - Ullner, Germany and by NIST - Quinn. This project featured a borosilicate crown glass and the NIST SRM 2830 Knoop Hardness standard. G. Quinn at NIST coorganized this project, and D. Smith performed the NIST experiments. The final report has been written and printed. This project proved that this methodology has serious between-laboratory inconsistency. More work to refine the experimental and analytical procedures is needed before standardization should be considered.

Quantitative Microscopy II, organized by NPL - Morrell, England and CTK - Dortmans, the Netherlands. This project investigated volume fraction second phase, porosity, and manual *versus* automatic image analysis. Ms. H. Moupas and G. Quinn at NIST participated. The final report has been printed. This project showed that AIA results are often less precise than manual methods, that much time was spent by the participants in optimizing the images, and that computer software nuances contributed to the scatter.

Fracture Toughness V, organized by EMPA - Kübler, Switzerland. This project featured an innovative simple method to precrack specimens with a razor blade and diamond paste. Mr. Quinn and Dr. Xu of NIST participated. Mr. Kübler is writing the final report. It appears that this simple means of producing a sharp notch is very effective. This method probably will be on a fast track for standardization.

Impacts:

Test method research at NIST evolves into VAMAS prestandardization round robins, to ASTM standards, to NIST SRM's, and eventually into worldwide ISO standards. Tangible benefits include significant cost savings to USA industry. For example, over $1M per year is saved by the USA by the use of standardized bend bars. The standards are being combined in materials specifications, such as the two new ASTM Committee F-04, specifications for zirconia or alumina for surgical implants. Standards also convert research procedures into mature engineering practices. For example, the C-28 fractographic analysis standard, C 1322, codifies what heretofore had been a highly interpretive art. C 1322 now is used as a teaching aid in courses at several universities and by a course offered by the American Ceramic Society. New scientific knowledge has emerged from prestandardization work such as the entirely new concept for brittleness which was discovered during our conventional hardness prestandardization research.

Publications:

Forty-eight reports and papers have been written to document the progress in this project. These have ranged from papers summarizing progress in standardization activities in general, to detailed papers on test methods and procedures, to round robin summaries. Seven papers were written this year:

J. Swab and G.. Quinn, "Effect of Precrack "Halos" on KIc Determined by the Surface Crack in Flexure Method," J. Am. Ceram. Soc., 81 [9] 2261-68 (1998). Also Publ. as U. S. Army ARL TR 1575, December 1997.

G. Quinn, J. Salem, I. Bar-On, and M. Jenkins, "The New ASTM Fracture Toughness of Ceramics Standard: PS 070-97," to be publ. Ceram. Eng. and Sci. Proc., 1998.

S. Scherrer, R. Kelly, G. Quinn, and K. Xu, "Fracture Toughness (KIc) of a Dental Porcelain Determined by Fractographic Analysis," J. Dental Res., 77, 1998, pp 656-663.

C. Ullner and G. Quinn, "Round Robin on Recording Hardness," VAMAS Report #33, BAM, Berlin, February 1998.

G. Quinn, "Hardness Testing of Ceramics," Advanced Materials and Processes, August 1998, pp. 23 - 27.

S. Scherrer, R. Kelly, G. Quinn, and K. Xu, "Fracture Toughness (KIc) of a Dental Porcelain Determined by Fractographic Analysis," proceedings of the 1998 IADR Conference, Nice, France, June 1998,

G. D. Quinn, M. Jenkins, J. Salem, and I. Bar-On, "Standardization of Fracture Toughness Testing of Ceramics in the United States," proceedings of the 3rd PAC RIM conference, Kyongju, Korea, September 21, 1998.

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Residual Stress Measurements

Principal Investigators: Linda M. Braun, Grady S. White, and Lawrence H. Robins

Technical Objective:

The objective of this project is to develop measurement procedures, using micro-Raman and luminescence spectroscopy, to evaluate quantitatively localized residual stresses that can control and influence mechanical, electrical, and optical properties of materials.

Technical Description:

Raman spectra are generated by the interaction of light with phonon modes in the unit cell. Consequently, stress induced changes in unit cell symmetry will cause shifts in Raman peak position and intensity. Stress is correlated with shifts in the Raman peak position as a function of a known externally applied load; changes in stress as small as 10 MPa can be detected. The phonon deformation potential terms must be determined in order to relate quantitatively stress to peak shift. In a similar manner, stresses in alumina cause shifts in the impurity Cr^{3+} luminescence line. We have used both an *in situ* micro-Raman technique and photoluminescence, with lateral resolution of ~6 μm, to probe stresses/strains in thermal barrier coatings (TBC's).

External Collaborations:

Modeling of the effect of stress on Raman spectra is being investigated in collaboration with Dr. Michael I. Bell of the Naval Research Laboratory (NRL). Stress effects on the reliability of thermal barrier coatings are being examined with M. Lance, M. Ferber, and A. Haynes at Oak Ridge National Laboratory (ORNL).

Planned Outcomes:

This work has demonstrated that techniques need to be developed to separate compositional variations from stress effects on peak shifts in Raman spectroscopy. Anticipated outcomes of this work include 1) a procedure combining luminescence and Raman spectroscopy to separate compositional and stress induced shifts in peak positions, and 2) an understanding of how thermal cycling develops stresses in TBC's.

Accomplishments:

Raman Stress Analysis: Hydrostatic Calibration Line vs. Phonon Deformation Potential
Comparisons have been made of two technical approaches for stress measurements based on the peak shifts associated with micro-Raman spectra. Stress values were obtained from evaluation of the

relationship between peak shift and stress determined by both a single line hydrostatic calibration and by evaluation of the phonon deformation potential terms. Single crystal sapphire and polycrystalline alumina were used to compare the two approaches. We have shown that for biaxial loading perpendicular to the c-axis in sapphire, the (0001) orientation, the hydrostatic analysis gives reasonable stress values. For biaxial loading in other orientations, the hydrostatic approach is inadequate. We have also shown that stresses for known off-axis crystal orientations can be evaluated using the phonon deformation potential approach.

Thermal Barrier Coatings

We have measured Raman spectra and photoluminescence (PL) spectra in two types of TBCs; physical vapor deposited and air plasma sprayed. The physical vapor deposited (PVD) specimens had been thermally cycled prior to spectroscopic investigation. The plasma sprayed specimens had no prior thermal treatment. Optical microscopy showed that the air plasma sprayed specimens had very rough surfaces, whereas the physical vapor deposited specimens were very smooth. In addition, Raman measurements were made on three powders of different mass fractions of yttria content: 0 %, 4.5 %, and 6.5 %.

Photoluminescence measurements of the thermally grown oxide scale between the bond coat and the zirconia thermal barrier layer showed the presence of a uniform residual stress in all specimens. Analysis of the stress value varied depending upon the assumptions used for the degree of texture in the alumina scale layer. Assuming the scale was untextured, PL measurements showed the presence of an 2.0 GPa compressive residual stress in the plane of the scale and no residual stress perpendicular to the plane. These values varied in both magnitude and direction if texture was assumed in the analysis. At this time we are attempting to measure the degree of texture in the oxide scale.

Raman measurements of the surface of these coatings showed a uniform peak shift in the Raman spectra of zirconia with 6.5 % yttria. This shift was uniform from specimen to specimen and within individual specimens. If attributed solely to residual stresses, this shift corresponded to a compressive biaxial stress of approximately 6.5 GPa. Comparison of Raman spectra of these coatings with spectra obtained from the powders showed that some, or perhaps all, of the shift could be attributed to yttria segregation within the zirconia coatings. High resolution TEM will be used to evaluate the extent of yttria segregation in these coatings.

Air Plasma Sprayed TBCs

These specimens have no prior heat treatment; therefore, no thermally grown oxide scale was expected. Consistent with this expectation, PL measurements of these specimens gave no indication of the presence of an alumina scale. Raman measurements of the coating surface showed much more variability than was observed in the PVD specimens. Shifts corresponding to 30 MPa up to 100 MPa were observed at various locations on the specimens. However, the average stress in plane value in each of the specimens was approximately zero, a result which is consistent with the lack of residual stress build up in TBC's that have not experienced thermal treatment.

Publications:

Linda M. Braun and Grady S. White, "Raman Stress Evaluation: Hydrostatic vs. Biaxial Calibration," submitted to Journal of the American Ceramic Society.

Program Title: Mechanical Properties of Brittle Materials

Project Title: Test Development for Aluminum Nitride Electronic Substrates

Principal Investigators: Jay S. Wallace and Edwin R. Fuller, Jr.

Technical Objective:

The primary objective of this research is to develop standard test methods for measuring strength and mechanical properties of aluminum nitride (AlN) and other thin substrate materials used in electronic packaging. A principle requirement of the test techniques is that they be able to measure the properties of the material in the condition in which the material is utilized, without further sample preparation or grinding in order that production materials can be tested.

Technical Description:

Development of highly reliable substrate materials requires the characterization of mechanical properties for materials which are fabricated with new powders and compositions. Unfortunately, the standardized techniques for evaluating strength, three- and four-point bending of 3 mm - 4 mm thick bar samples, are incompatible with the geometry of the 0.5 mm - 1 mm thick tape-cast plates used as substrates. In order to meet the thickness requirements for conventional strength testing, the sample fabrication conditions would have to be extensively modified, raising questions whether the materials being tested are representative of production substrate materials. Furthermore, machining required by the standard test protocols can either introduce new flaw populations into the material or remove existing flaw populations, resulting in test data that do not represent the properties of the in-service material. In this project a ring-on-ring technique is being considered for testing electronic substrate materials in their in-service condition without further sample preparation.

External Collaborations:

This research is part of the *Japan-U.S. Research Collaboration in Aluminum Nitride* for pre-competitive research in the development of AlN materials. It is a four-way collaboration. Dow Chemical Company of Midland, Michigan provides AlN powder to Toshiba=s Research and Development Center in Japan to make test specimens. NIST develops and conducts tests for characterizing the mechanical behavior of AlN substrates, and Japan=s National Industrial Research Laboratory of Nagoya (NIRIN) is responsible for processing studies and microstructural characterization.

Planned Outcomes:

The major outcomes expected from this research are: (1) a standard ring-on-ring strength test for thin ceramic speciments, (2) development of testing methodologies for evaluating structural properties and reliability of thin ceramic substrate materials in their in-service condition, and (3) an

understanding and characterization of the microstructural factors that control the properties in these materials.

Accomplishments:

Since the ring-on-ring fixtures were designed and fabricated, the four participants in the program have participated in three AlN strength round robin tests. Results from the first round robin identified some difficulties in the design and fabrication of the testing fixture. The fixture problem which was identified was confirmed with finite element calculations. The second round robin identified interactions between the fixtures and the sample which lead to laboratory to laboratory irreproducibility. The third round robin again raised concerns about the test fixture and sample to fixture interactions. These sample to fixture interactions were experimentally confirmed using samples with strain gauges. Further strength testing and strain measurements of samples with compliant layers between the fixture and sample have shown improved laboratory to laboratory consistency.

Microstructural evaluation has shown that the second phase distribution and composition in these materials can vary greatly, depending on the starting powders and processing conditions. However, the effect on strength seems to be slight unless there is a pronounced cracking tendency in the second phase. A near-surface layer, which would have been removed by grinding in conventional testing, was shown to have a strong effect on the strength of the as-fired samples. Therefore, it is important that this layer not be removed so that the true in-service property is determined.

The results of this collaboration were presented at the International Symposium on Aluminum Nitride Ceramics, held in Tokyo, Japan on March 11-13, 1998.

Publications:

J.S. Wallace, E.R. Fuller, Jr., F. Ueno, M. Kasori, T. Ohji and W. Rafaniello, "Strength Measurement Metrology For AlN Substrates," Submitted to Proceedings of the International Symposium on Aluminum Nitride Ceramics

PROGRAM TITLE: Mechanical Properties of Brittle Materials

PROJECT TITLE: Test Development for Membrane Materials

Principal Investigators: Ralph Krause, Jr., Tze-jer Chuang, and William E. Luecke

Technical Objective:

The objective of this is to develop measurement techniques for the mechanical properties of dual purpose oxygen conducting ceramic materials.

Technical Description:

Testing methods for measuring mechanical properties of small, brittle tubular specimens at elevated temperatures and in controlled environments are evaluated, improved, and refined. Key mechanical properties affecting design including strength, residual stress state, and elastic modulus are evaluated. Properties affecting lifetime and reliability, including Weibull properties, residual stress state, subcritical crack growth behavior, and fracture toughness are evaluated. Special considerations are needed due to the interplay between component geometry, compositionally driven residual stress, and environmental history. Efforts have focused on an O-ring testing configuration for characterizing strength and a C-ring configuration for evaluating Young's modulus. Existing candidate materials are evaluated to validate testing techniques and to provide preliminary data to facilitate design and fabrication of reactor components. Finite element and analytical analyses support the test method development. Coupled diffusional equations with misfit stress calculations aid in evaluating the influence of the compositionally driven residual stress state.

External Collaborations:

Timothy Armstrong, Pacific Northwest National Laboratory, has collaborated in this work.

Planned Outcomes:

We expect to develop an O-ring strength test and a C-ring test for elastic modulus for tubular ceramic components.

Accomplishments:

Tests have begun that will provide critical data for standardization work for a tubular specimen for ceramic strength and reliability evaluation. Work also began on characterizing slow crack growth and reliability of zirconia doped with yttria at fuel cell temperatures.

PHASE EQUILIBRIA FOR CERAMICS AND METALS

Thermodynamic phase equilibrium data, which indicate the identities and quantities of the final, stable products of any given process, are essential tools for developers and manufacturers of engineering materials. The Phase Equilibria Program encompasses not only data compilations and experimental measurements of phase equilibria, but also development of thermodynamic and first-principles models which describe the underlying basis of the equilibria. In addition, several projects go beyond the direct graphical representation of equilibria to include characterization of the physical and crystallographic properties of the constituent phases, or to incorporate the equilibrium information into kinetic models of non-equilibrium processes. MSEL phase equilibrium work includes the following main projects:

High Temperature Superconductors

The objective of this activity is to conduct experimental studies of copper-based materials with emphasis on regions and conditions pertinent to the improved manufacture of bulk superconducting wires and tapes. Efforts have been largely directed to the Bi-Sr-Cu-Ca-O systems which are currently of greatest commercial interest. The successful processing of wires with high current-carrying capacities and excellent superconducting properties is known to require the *in situ* coexistence of high quality superconducting solid plus a liquid phase to induce texturing and grain alignment. The phase diagram work is therefore directed toward determining the location in composition-P-T space of the primary crystallization fields of the BiSCCO superconductors; that is, the regions where only 2 phases are present - the superconducting solid plus a liquid. Considerable efforts are also directed to developing graphical and other practical methods for end users of the complex data. This research is carried out in close collaboration with the U.S. Department of Energy (DOE) Superconductivity Program for Electric Systems and its participating national laboratories.

Dielectrics for Wireless Communications

Dielectric ceramics are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (e.g., resonators, bandpass filters, circulators). The required properties for the ceramic materials include high dielectric constant, minimal dielectric loss, and essentially zero temperature dependence of dielectric properties. Knowledge of phase equilibria relations is important because all ceramic components are processed as controlled mixtures to achieve temperature stabilization; furthermore, the existence of previously unknown compounds with potentially useful properties may be revealed. This research activity emphasizes experimental determination of ternary (or higher) phase diagrams that contain one or more components or compounds that exhibit useful properties, and the correlation of chemical composition, atomic arrangement, and dielectric performance within each system. The experimental work includes synthesis, structural analysis, determination of phase relations, and microwave characterization (*via* collaborators at NIST/Boulder) of dielectric properties.

Computational Studies of Ferroelectrics and Dielectrics

Ferroelectric ceramics exhibit unique dielectric properties that are widely exploited to produce multilayer capacitors and transducers. Related ceramic systems are useful as high performance dielectric resonators for wireless communications. The electronic properties of these materials are strongly dependent on the exact ordering patterns adopted by the atoms within the ceramic material; only certain, precise arrangements result in electronically useful properties. Understanding of why and how these particular arrangements occur is needed by industry to improve processing control, reduce the associated costs, and enable the rational design of improved materials. The objective of this research activity is to develop and apply computational tools to model the structural behavior of these important materials as a function of chemical composition and temperature. The work is carried out using first principles phase diagram calculations, including the Ising model and Monte Carlo methods.

NIST-ACerS Phase Equilibria Diagrams Database

The objective of this project is to prepare and publish evaluated phase equilibria data for the industrial and academic communities. Technical evaluation of original literature containing phase diagram information is carried out under NIST supervision. The preparation of the evaluated diagrams for dissemination as the reference series, Phase Equilibria Diagrams (formerly Phase Diagrams for Ceramists), is conducted at NIST in collaboration with on-site personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by the Society from industry, academia, and individuals. The collaboration with ACerS to provide technically evaluated phase diagrams for the ceramics industry has continued for more than sixty years.

Solidification Path for Multicomponent Superalloys

This project develops a thermodynamic data base for Ni-base superalloys, which is then used to calculate phase equilibrium information and subsequently the alloy solidification behavior. This information is incorporated into commercial software used by the aerospace industry to analyze the casting of numerous multicomponent alloy compositions. The thermodynamic and solidification models predict the identity and volume fraction of all phases present in the casting microstructure, as well as other important information such as enthalpy and liquid density as functions of temperature. This approach greatly reduces the need for experimental measurements of alloy solidification behavior.

PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: Computational Studies of Ferroelectrics and Dielectrics

Principal Investigators: B.P. Burton and E.J. Cockayne

Technical Objective:

The objective of this project is to elucidate the role of order-disorder and ferroelastic phenomena in determining the phase relations and physical properties of technologically important ferroelectric and dielectric ceramics. These ceramics are used to fabricate multilayer capacitors, transducers, and dielectric resonators for wireless communications.

Technical Description:

The ferroelectric, dielectric, magnetic, and transport properties of ceramic systems are typically sensitive functions of the state of cation order; only certain, precise arrangements result in electronically useful properties. Improved understanding of why and how these particular arrangements occur is needed by industry to improve processing control and reduce the associated costs. This research effort involves the use of first principles phase diagram (FPPD) calculations to predict cation ordering phenomena, and critical experiments are performed to test the predictions. An additional technical objective is to benchmark various techniques for calculating the formation energies on which FPPD calculations are based.

External Collaborations:

Collaborators in this work include:

J. Fontan (Univ. Autonoma, Barcelona, Spain): FPPD calculations of the NaCl-KCl, NaBr-KBr, and NaI-KI phase diagrams;

G. Ceder and A. Van Der Ven (MIT): issues related to Ising model calculations;

D.M. Teter (UVA): high pressure phase equilibria in SiO_2;

G. Kern (Technical University, Vienna): application of the Vienna ab-initio simulation package (VASP) pseudopotential code to calculate structure energies for FPPD calculations for ordered supercells in the systems $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN);

K. M. Rabe and Ph. Ghosez (Yale): pseudopotentials and first-principles methods for calculating total energies and linear responses; and

J. B. Aidun, T. V. Russo and K. Leung (Sandia): FPPD calculations for the $PbTiO_3$-$PbZrO_3$ system.

Planned Outcomes:

The intended outcome of this research is to predict ordering behavior in technologically important, complex oxide systems, with the objectives of: (1) minimizing the experimental work necessary to elucidate phase relations; (2) perfecting theoretical techniques; (3) optimizing processing strategies for these materials; and (4) predicting the existence of new, potentially useful ordered phases.

The inclusion of degrees of freedom, derived from ionic motion, in the first-principles models will facilitate simulation and physical understanding of important electronic properties. For example, the ferroelastic transitions in PZT, experimentally associated with large piezoelectric effects, can be simulated as a function of temperature and strain. By adding the effects of time-varying external fields to the models, dielectric response as a function of temperature and frequency can be modeled in systems such as BST ($(Ba,Sr)TiO_3$).

Accomplishments:

Empirical calculations were used to model cation ordering behavior, particularly short-range order, in the widely used multilayer capacitor material $Pb(Mg_{1/3}Nb_{2/3})O_3$. Full potential VASP total energy calculations have been performed for 19 different structures in the pseudobinary system $PbNbO_3$-$PbMgO_3$. The results will be used to fit a cluster expansion Hamiltonian, which will be used as input for a FPPD calculations. Major results of these calculations are:

- Analysis of empirical Hamiltonians has identified essential interactions for stabilizing the 1:2 ground state that is observed in $Ba(Zn_{1/3}Ta_{2/3})O_3$, and the transition sequence: 1:2 → 1:1 → DIS, which is observed in $Ca(Ca_{1/3}Nb_{2/3})O_3$.

- Fully relaxed, full-potential VASP structure energies were calculated for 19 different ordered structures in the system $PbNbO_3$-$PbMgO_3$. These will be used as a basis for FPPD calculations (Monte Carlo simulation) of cation order-disorder phenomena in $Pb(Mg_{1/3}Nb_{2/3})O_3$.

Publications:

B.P. Burton, R.P. McCormack, G. Ceder, R.L.B. Selinger, G. Kresse, and J. Hafner, "Modeling Cation Ordering in Some $A(B'_{1/3}B''_{2/3})O_3$ Perovskites", in First-Principles Calculations for ferroelectrics, R.E. Cohen Ed. AIP Conference Proceedings 436, 20-, (1998).

B. Burton, Empirical Cluster Expansion Models of Cation Order-Disorder in $A(B'_{1/3}B''_{2/3})O_3$ Perovskites, Submitted, Phys. Rev. B (1998).

B. Ravel, E. Cockayne and K.M. Rabe, The Local Structure of Ferroelectric Ge_xTe, Synchrotron Radiation, in press.

PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: Dielectric Oxides for Wireless Communications

Principal Investigator: T.A. Vanderah

Technical Objectives:

The objective of this project is to determine phase equilibria and structure-property relations in complex titanate- and niobate-based systems of interest as dielectric oxides in wireless communications systems.

Technical Description:

Dielectric ceramics are used to fabricate a variety of components in cellular communications circuits that store, filter, and/or transfer electromagnetic energy with minimal loss (*e.g.*, resonators, bandpass filters, circulators). The required properties for the ceramic materials include high dielectric constant, minimal dielectric loss, and essentially zero temperature dependence of dielectric properties. Knowledge of phase equilibria relations is important because all ceramic components are processed as mixtures to achieve "compensation", *i.e.*, a net overall zero temperature coefficient. The approach taken by the phase equilibria group emphasizes experimental determination of previously unknown ternary (or higher) oxide systems containing one or more components or compounds that exhibit useful properties as dielectric ceramics for microwave communications. Technical efforts include synthesis, structural analysis, determination of phase relations, and characterization (*via* collaborative efforts) of dielectric properties. Systems of current interest include $BaO:Fe_2O_3:TiO_2$, $SrO:TiO_2:Nb_2O_5$, $CaO:Al_2O_3:Nb_2O_5$, $SrO:Al_2O_3:Nb_2O_5$, $CaO:TiO_2:Ta_2O_5$, $CaO:TiO_2:Nb_2O_5$, and $BaO:TiO_2:Ta_2O_5$.

External Collaborations:

Characterization of dielectric properties is accomplished by collaborations with UCLA (Electrical Engineering Department) and NIST staff in Boulder (RF Technology Division). Productivity in this project is enhanced by interaction with the Geology Department at the University of Maryland in the form of small contracts that support undergraduate and graduate students to work as technical assistants at NIST. Active industrial collaborations exist with Lucent Technologies, Trans-Tech, Inc., and Trak Ceramics.

Planned Outcomes:

Accurate, experimentally determined phase diagrams will be established that are of immediate interest to U.S. industry involved in the production of ceramics for wireless communications systems. Diagrams that include dielectric property data will indicate the chemical identities of new, potentially useful compounds as well as the compositions of equilibrium mixtures that can be processed as ceramics with controlled properties.

Accomplishments:

New detailed characterizations of phases found previously in the $BaO:Fe_2O_3:TiO_2$ system has continued. Single crystals of $Ba_6Fe_{45}Ti_{17}O_{106}$ and $BaFe_{11}Ti_3O_{23}$ were obtained as major and minor co-products, respectively, by slow-cooling an off-stoichiometric $BaO:Fe_2O_3:TiO_2$ melt. The former compound exhibits variable stoichiometry, $Ba_6Fe_{48-x}Ti_{14+x}O_{106}$, with the Fe:Ti ratio dependent upon the partial pressure of oxygen. The value of x corresponds to the equivalents of reduction that occur to maintain electroneutrality as the Ti content increases. When prepared in air, this phase occurs at x=3 with the stoichiometry $Ba_6Fe_{45}Ti_{17}O_{106}$, while in 100 % oxygen the x-value approaches zero with the resulting stoichiometry $Ba_6Fe_{48}Ti_{14}O_{106}$ (all Fe^{3+} and Ti^{4+}). The structures of $Ba_6Fe_{45}Ti_{17}O_{106}$ and $BaFe_{11}Ti_3O_{23}$ were solved using single crystal x-ray diffraction methods. $Ba_6Fe_{45}Ti_{17}O_{106}$ was prepared in polycrystalline form and further structural details, including accurate Fe/Ti occupancy factors, were determined by a combined refinement using neutron and synchrotron powder diffraction data. Both compounds adopt *8L* close-packed structures built from alternating *ccp* and *hcp* [O,(Ba,O)] layers stacked along the *a*-direction with a $(ch)_4$ repeat sequence. Both structures feature octahedral sites occupied by a mixture of Fe and Ti as well as tetrahedral sites occupied by Fe^{3+}; the structural formulas are $^{XII}Ba_6{}^{IV}Fe_6{}^{VI}(Fe_{39}Ti_{17})O_{106}$ and $^{XII}Ba^{IV}Fe_2{}^{VI}(Fe_9Ti_3)O_{23}$ (Roman numerals denote cation coordination numbers). Both compounds are partially reduced; the former contains three moles of Fe^{2+} (or Ti^{3+}) per formula unit, the latter, one. The formation of Fe^{2+} is considered more likely than Ti^{3+}, but could not be experimentally confirmed. $BaFe_{11}Ti_3O_{23}$ is apparently metastable in air when cooled from above the solidus, and could not be prepared as a polycrystalline sample. Indexed experimental x-ray powder diffraction data for $Ba_6Fe_{45}Ti_{17}O_{106}$ are given. Polycrystalline samples of this compound were used to measure its magnetic and electrical properties. The magnetic behavior of $Ba_6Fe_{45}Ti_{17}O_{106}$ above room temperature up to 1073 K was found to obey the Curie-Weiss law, which indicated a small effective molar magnetic moment (34 μ_B for $Ba_6Fe_{45}Ti_{17}O_{106}$) and a large negative temperature intercept (-806 K). Electrical resistivity measurements between room temperature and 120 K revealed nonmetallic behavior with an activation energy on the order of 0.17 eV. At 347 MHz under ambient conditions, $Ba_6Fe_{45}Ti_{17}O_{106}$ exhibited a relative permittivity of 24 and a dielectric loss tangent of 0.10.

Experimental x-ray powder diffraction patterns and refined unit cell parameters for two barium hollandite-type compounds, $Ba_xFe_{2x}Ti_{8-2x}O_{16}$, with x = 1.143 and 1.333, were determined and documented. Compared to the tetragonal parent structure, both compounds exhibit monoclinic

distortions that increase with Ba content. The x-ray powder patterns for both phases contain a number of broad, weak superlattice peaks attributed to ordering of the Ba^{2+} ions within the tunnels of the hollandite framework structure. According to the criteria available in the literature, the observed positions of the $(0k1)/(1k0)$ superlattice peaks are consistent with the nominal x-values of both compounds, and the k values calculated from the corresponding d spacings suggest that the Ba ordering within the tunnels is commensurate for x=1.333 and incommensurate for x=1.143. High-temperature X-ray diffraction data indicated that the x=1.333 compound undergoes a monoclinic→tetragonal phase transition between 310 °C and 360 °C.

Experimental determinations of the $CaO:Al_2O_3:Nb_2O_5$ and $SrO:Al_2O_3:Nb_2O_5$ systems were initiated. The former appears to contain a single ternary compound, Ca_2AlNbO_6, which adopts a fully 1:1 ordered double-perovskite structure with a $CaTiO_3$-type distortion. This compound is potentially useful as a lower-permittivity, higher-Q ceramic for high-frequency applications to replace $Ba_3ZnTa_2O_9$, which is undesirable owing to the high cost of Ta_2O_5 raw material. Measurements of the dielectric properties of Ca_2AlNbO_6 and the compounds that occur in equilibrium with it are in progress. In the sister system $SrO:Al_2O_3:Nb_2O_5$, the analogous ternary compound Sr_2AlNbO_6 was found to occur, in addition to a new phase between this compound and SrO. Sr_2AlNbO_6 adopts an undistorted 1:1 ordered double-perovskite structure, and may exhibit potentially useful properties that rival those of $Ba_3ZnTa_2O_9$.

Publications:

I.E. Grey, C. Li, L.M.D. Cranswick, R.S. Roth, and T.A. Vanderah, "Structural Analysis of the 6H-$Ba(Ti,Fe^{3+},Fe^{4+})O_{3-\delta}$ Solid Solution", J. Solid State Chem. **135**, 312-321 (1998).

I. Levin, L.A. Bendersky, T.A. Vanderah, R.S. Roth, and O.M. Stafsudd, "A Series of Incommensurately Modulated $A_nB_nO_{3n+2}$ Phases in the $SrTiO_3$–$Sr_2Nb_2O_7$ Quasibinary System", *Mat. Res. Bull.* 33(3), 501-517 (1998).

L.A. Bendersky, T.A. Vanderah, and R.S. Roth, "Structural Study of a Group of Magnetic-Dielectric Oxides in the $BaO:TiO_2:Fe_2O_3$ System. Part I. High-Resolution Electron Microscopy", *Phil. Mag. A*, in press.

T. Siegrist, T.A. Vanderah, A.P. Ramirez, R.G. Geyer, and R.S. Roth, "Crystal Structure and Properties of $Ba_5Fe_4Ti_{10}O_{31}$", *J. Alloys Compounds* **274**(1-2), 169-179 (1998).

J.M. Loezos, T.A. Vanderah, and A.R. Drews, "Barium Hollandite-Type Compounds $Ba_xFe_{2x}Ti_{8-2x}O_{16}$ with x= 1.143 and 1.333", *Powder Diffraction*, in press.

T.A. Vanderah, W. Wong-Ng, B.H. Toby, V.M. Browning, R.G. Geyer, R.D. Shull, and R.S. Roth, "Characterization of Ternary Compounds in the $BaO:Fe_2O_3:TiO_2$ System: $Ba_6Fe_{45}Ti_{17}O_{106}$ and $BaFe_{11}Ti_3O_{23}$", *J. Solid State Chem.*, in press.

I. Levin, L.A. Bendersky, and T.A. Vanderah, "Crystal Structure of the Layered $Sr_n(Ti_{1-y}Nb_y)O_{3n+2}$ Compounds. Part II. TEM Study of the $Sr_n(Ti,Nb)_nO_{3n+2}$ Structures", submitted to *Phil. Mag.*

PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: High Temperature Superconductors

Principal Investigators: Winnie Wong-Ng and Lawrence P. Cook

Technical Objective:

The objective of this project is to develop pertinent phase equilibrium diagrams for the high temperature superconductor materials used in bulk conductors (tape and wire). The current research focus is on the location of the primary phase field of the Pb-doped 2223 ([Bi,Pb]-Sr-Ca-Cu-O, to ≈110 K) phase, and the effect of Ag impurities on this crystallization field. A parallel effort utilizes the data to investigate phase formation of the Pb-2223 phase.

Technical Description:

The Bi(Pb)-Sr-Ca-Cu-O (BiSCCO) superconducting tapes prepared by the powder-in-tube (PIT) technique have demonstrated the potential for supporting high critical currents in high magnetic fields. These tapes offer a promising route to the industrial scale fabrication of long length, high quality superconducting cables. Phase equilibria data are essential for guiding the processing of high-T_c phases. In order to optimize the PIT technique, extensive data on the phase equilibria of BiSCCO materials are needed, including accurate experimental data on the phase relationships and locations of the primary phase fields of the superconductors. In previous years, efforts have concentrated on the location of the primary phase field of the Pb-free 80 K 2212 (Bi:Sr:Ca:Cu) phase, and the portion of the crystallization field of the Pb-2223 phase that coexists with the Pb-2212 phase. This year, experimental data mapping the entire primary phase field of the Pb-2223 phase have been obtained. In addition, the effect of Ag on this primary phase field, and on the phase formation of the Pb-2223 phase, has been investigated. Analytical techniques used include X-ray diffraction and differential thermal analysis. Additionally, melts were captured using a wicking technique, and their compositions were analyzed using scanning electron microscopy and energy dispersive x-ray spectrometry.

External Collaborations:

This project is partially supported by the DOE Superconductivity Program for Electric Systems which emphasizes development of bulk conductors (wires and tapes). Our NIST collaborators include Anthony Kearsley and Craig Lawrence of the Applied Mathematics Division. Ongoing external collaborations exist with the other national laboratories participating in the DOE program (ORNL, LANL, ANL) to exchange information and/or samples, and to combine complementary expertise.

Planned Outcome:

The experimentally determined primary phase field of the Pb-2223 phase with and without Ag as a component will be modeled and appropriately documented for use by materials producers. NIST staff will work with users of this complex data set so that the desired data (phase assemblages as a function of temperature, atmosphere, and overall chemical composition) can be extracted for commercial application. Wire producers will use this information to improve processing control of wires with optimized electrical properties.

Accomplishments:

(1) We have completed the study of the subsolidus phase compatibilities of the Pb-2223 phase in the pertinent regime of the 5-component (without Ag) and 6-component (with Ag) BiSCCO systems. In each case, a total of 29 self-consistent five-phase volumes were found with the Pb-2223 phase as a participant. The 29 melt compositions obtained from these five-phase assemblages were used to construct the primary phase field of the Pb-2223 phase. These multi-dimensional "volumes" can best be modeled using the convex hull technique. All data points were found to lie on or very near to a convex hull, and can be described using a matrix equation. A given composition can then be determined to lie within or outside the Pb-2223 primary phase field by applying this equation. The addition of Ag did not appear to significantly alter the Pb-2223 subsolidus relationships. However, the initial melting temperatures of the multiphase volumes were lowered by 2 °C to 25 °C. Ag was found to enter the liquid with a mole fraction in the range from 1 % to 6 %. The presence of Ag decreases the Pb-content of the liquid significantly.

(2) We have characterized the liquids that are associated with the formation of the 2223 phase from a precursor sample with the composition $Bi_{1.8}Pb_{0.4}Sr_2Ca_{2.2}Cu_3O_x$. The initial liquid that forms from this precursor mixture is metastable because the temperature and composition are different from that of the initial melts produced from extensively annealed samples. This metastable liquid participates in a chemical reaction to produce the high T_c Bi(Pb)-2223 phase. The phase formation equation is the same with and without Ag when the sample is annealed under air, but is different under an atmosphere of 7.5 % O_2. Under all four conditions investigated in this study, both metastable and stable liquids can assist the phase formation and grain growth of Bi(Pb)-2223, depending on the temperature at which the sample is annealed. Implications for processing of the high T_c 2223 phase starting from a given precursor composition have been published (ref. 3 below).

Publications:

W. Wong-Ng, L.P. Cook, F. Jiang, W. Greenwood, U. Balachandran and M. Lanagan, "Subsolidus-Phase Equilibria of Coexisting High-T_c Pb-2223 and 2212 Superconductors in the (Bi,Pb)-Sr-Ca-Cu-O System under 7.5% O_2," J. Mater. Res. 12 (11) 2855-2865 (1998).

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PROGRAM TITLE: Phase Equilibria for Ceramics and Metals

PROJECT TITLE: NIST-ACerS Phase Equilibria Diagrams Database

Principal Investigators: M.A. Clevinger and T.A. Vanderah

Technical Objective:

The objective of this project is to maintain and develop a state-of-the-art database of critically evaluated ceramic phase equilibria data for industrial and academic customers.

Technical Description:

Technical evaluation of phase diagrams obtained from the literature is carried out under NIST supervision. Preparation of evaluated diagrams for publication and dissemination is carried out at NIST by direct collaboration with personnel of the American Ceramic Society (ACerS). The ACerS personnel are primarily supported by funds raised by the Society from industry, academia, and individuals. The collaboration of more than 60 years represents an agreement with ACerS to provide evaluated phase diagrams for the ceramic industry. The phase diagrams are supplied either in printed form or in computerized versions, and are distributed through the ACerS.

External Collaborations:

American Ceramic Society research associates (Christina Cedeno, Evans Hayward, and Nils Swanson) collaborate closely with NIST staff to computerize and produce the phase diagram publications developed in this cooperative program. Drs. Robert Roth and Helen Ondik, and Mr. Howard McMurdie serve as editors or consultants for various parts of the project.

Accomplishments:

The major area of activity has been on a monograph containing all known phase equilibria information relative to zirconium (Zr) and its compounds. This is the first phase diagram volume combining both old and new material covering systems for a single element. This monograph, edited by Helen Ondik and H. F. McMurdie will bring together new (500) as well as previously published (700) evaluated diagrams; it will also contain an appendix listing references containing phase equilibria information but not a plotted diagram.

A considerable amount of effort has been directed toward evaluation of the database structure and the formulation of a plan for overall modernization of the operation to stand-alone, PC-based desk-top publishing. Efforts were also directed towards correcting and improving the CD-ROM

containing all of the phase diagrams published through Volume 11. Corrected CD-ROM's were distributed to customers by ACerS.

Work was initiated on Volume XIII of the series Phase Equilibria Diagrams. This volume, edited by R.S. Roth and T.A. Vanderah, will contain phase diagrams pertinent to oxide systems. Publication is scheduled for Fall 1999.

Publications:

Phase Diagrams for Zirconium and Zirconia Systems, Edited by H.M. Ondik and H.F. McMurdie. ACerS, Westerville, Ohio, 1998, 525 pages.

Phase Equilibria Diagrams 1998 Cumulative Index--Volumes I-XII, Annuals '91-93, High T_c Manographs I-II, Zirconium and Zirconia Systems. Edited by M.A. Clevinger and C.L. Cedeno. ACerS, Westerville, Ohio, 1998, 295 pages.

SYNCHROTRON RADIATION CHARACTERIZATION

The availability of synchrotron radiation is resulting in major discoveries over a wide range of disciplines. The Synchrotron Radiation Program is a development and characterization effort which includes the operation of beam stations at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, the commissioning and operation of new beam stations at the Advanced Photon Source (APS) at Argonne National Laboratory in a collaborative arrangement called UNI CAT with the University of Illinois, Oak Ridge National Laboratory and U.O.P. Corporation, and a microstructural characterization effort in which NIST scientists, and researchers from industry, universities and other government laboratories perform state-of-the-art measurements on advanced materials.

At these facilities, a wide range of measurements is carried out. Scientific problems currently being addressed include microstructural characterization of ceramics and plasma-sprayed ceramic coatings, crystal perfection of a variety of basic and applied materials, the evolution of dislocation structures as a function of deformation, and the atomic-scale and the molecular-scale structures at surfaces and interfaces in polymeric, metal / semiconductor, catalytic, and other systems of technological importance.

The APS currently offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron x-ray sources of the 1980s and the early1990s. In the years to come the APS will supplant the NSLS as this nation's premier x-ray source. The APS beam lines, currently being commissioned by NIST at UNI-CAT, incorporate the newest technology which will not only enable NIST scientists to improve significantly our real-time x-ray microscopy, ultra-small-angle x-ray scattering, in situ x-ray topography and x-ray absorption fine structure (XAFS) capabilities, but will also offer opportunities for cutting-edge experiments in structural crystallography and time-resolved structural scattering, surface / interface scattering, diffuse scattering, and magnetic scattering. NIST scientists anticipate extending our present portfolio of characterization capabilities to include an even wider range of materials measurements of importance to materials scientists and to U.S. industry.

Experimental capabilities include:

- *In situ* studies of surface relaxation and phase transitions in approximate monolayer coverage in semiconductor crystals, buried interfaces, and multilayers; the brilliance at the APS will make it possible for the first time to monitor surfaces and interfaces *in situ* during MBE or CVD.

- Investigations of ceramics, coatings, and polymers; our sensitivity will be increased by a factor of 100 in ultra-small-angle x-ray scattering.

- Imaging of defects in semiconductor crystals, photonic materials, and superconducting crystals; real time imaging will become a practical reality at the APS and resolution will reach below 1 μm.

- Structure determination from single crystals or powders; time resolved studies during melting or phase transitions will become possible.

- Diffuse x-ray scattering determination of structures and the behavior of lattice imperfections in ceramics, metals, semiconductors, and superconductors.

- Determination of magnetic structure and defects in magnetic superlattices, high-T_C superconductors, and magnetic Compton scattering; the brilliance and circularly polarized x-ray beams will enable magnetic x-ray measurements that could never be made before.

- X-ray absorption spectroscopy in a reactive environment.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Beamline Operation and Development

Principal Investigators: Gabrielle Long, Andrew Allen, David Black, Hal Burdette, Dan Fischer, Lyle Levine, Richard Spal, and Joseph Woicik

Technical Objectives:

The technical objectives of this project include the operation of two materials science x-ray beam stations (X23A2 and X23A3) at the National Synchrotron Light Source (NSLS), at Brookhaven National Laboratory for diffraction imaging, x-ray radiography, ultra-small-angle x-ray scattering (USAXS), x-ray absorption fine structure (XAFS) spectroscopy, and standing-wave x-ray measurements. NIST is also a partner in the operation of two additional beam stations (U7A and X24A) for materials science using ultra soft x-ray absorption measurements and soft x-ray standing-wave measurements of semiconductor surfaces and interfaces.

Another major technical objective is the commissioning and operation of five beam stations on Sectors 33 and 34 at the Advanced Photon Source (APS), at Argonne National Laboratory, together with NIST's Collaborative Access Team (CAT) partners [University of Illinois, Oak Ridge National Laboratory, and UOP Corporation]for high-resolution diffraction, USAXS, surface and interface scattering, x-ray diffraction imaging and microtomography, XAFS, diffuse scattering, x-ray microbeam diffraction and fluorescence, and coherent scattering.

Technical Description:

The Synchrotron Radiation Program involves the operation of beam stations at the NSLS and the commissioning and operation of beam stations with our CAT partners at the APS. Currently, more than 140 scientists per year from NIST, and from industry, universities and other government laboratories, come to the NIST advanced materials characterization beamlines at the NSLS to perform state-of-the-art measurements. In the future, some of our NSLS activities will be transferred to the APS, where the parameters of the source give us unique opportunities. Other NIST facilities, which make use of the properties of the NSLS source, will remain there.

The range of scientific problems currently being addressed at the NSLS includes: microstructure evolution during hydration of cements (see, "Characterization of Cements" under Other Programs), studies of bonding and bond lengths in strained semiconductor layers, damage in sapphire windows, surface characterization of joint replacement materials, tribochemical reactions on surfaces, orientation of lubricants on hard disk magnetic media substrates, and development of new

catalysts and biomaterials. The investigation of the formation of dislocation structures, which is a problem on which very little progress had been made over 50 years of effort, has enjoyed remarkable success in measuring the total line length of populations of dislocations, the presence of correlations

between dislocations, relaxation of dislocation structures at room temperature in aluminum, and the presence of dipole (and possibly higher) dislocation configurations.

External Collaborations:

Collaborators in this project include: Haydn Chen and T. C. Chiang, University of Illinois, Gene Ice and Ben Larson, Oak ridge National Laboratory, Robert Broach, UOP Corporation, H. Boukari and M. Harris, University of Maryland, G. Beaucage and D. Schaefer, U. of Cincinnati, R. Livingston, Federal Highway Administration.

Planned Outcome:

The APS offers a 100 to 10,000-fold increase in brilliance compared to the best synchrotron x-ray sources of today, and thus, in the years to come, the APS will supplant the NSLS in some areas as this nation's premier x-ray source. Five beam stations on sectors 33 and 34 of the APS wil be developed and maintained.

Accomplishments:

The USAXS capability that was at the NSLS was moved to the APS during 1998. Its overlap with visible light scattering and pinhole small-angle cameras has been increased significantly, and thus its ability to quantify microstructures in the micrometer range and in the nanometer range have both been improved. As one of the few SAXS instruments in the world for which a primary absolute calibration is available, the data from the NIST instrument serves an important role in setting scattering standards.

The high-resolution, monochromatic x-ray topography camera at the NSLS is the only dedicated monochromatic facility of its type in this country, and is the only instrument able to support experiments at the highest resolution. A new x-ray topography instrument, with increased sensitivity generally, and increased sensitivity to surface microstructures in particular, is currently being prepared for installation at the APS during 1999. At U7A, a refocussing mirror which produces a sub-millimeter spot has been installed. A sample manipulator and preparation/load lock chamber, which allows rapid sample entry as well as sample pre-treatment, has been installed. And finally, a focussing wavelength dispersive detection system was brought on line. This last system effectively reduces the scattered light and fluorescence backgrounds to nearly zero.

In the area of instrument development for the APS, the components for the beam conditioning table for the high resolution x-ray diffraction hutch have been installed and commissioned. The newly constructed four-reflection USAXS, including the new silicon optics, offer an increase in resolution, a decrease in background, and very important improvement in signal-to-noise. This new instrument, which operates at theoretical levels, was tested during 1998 in a wide range of commissioning experiments. The operations phase will begin, for UNICAT members, in early 1999.

All of the instrumentation for the bending magnet beam line has either been received or is in procurement. The radiation enclosures passed safety approval in early 1998. The x-ray topography procurement is complete and the XAFS procurement is complete. It appears that the installation of the scientific instruments will precede the commissioning of the monochromator and mirrors in this case.

Procurement for Sector 34 apparatus has begun. Specifications for the sector 34 radiation enclosures are under development. Prototype Kirkpatrick-Baez mirrors and Fresnel lens optics are currently being evaluated.

Impacts:

The availability of synchrotron radiation is resulting in major discoveries over a wide range of research in advanced materials science and processing. Studies of the relationship between microstructured development in hydrating cements and the morphology of additives are key to the development of more effective additives for this important class of material. Fundamental measurements of dislocation formation as a function of strain in single crystal materials are leading to new constitutive laws for future redevelopment of finite element modeling codes. Studies of defect formation in sapphire windows enable improved assessment of the surface and subsurface integrity of these materials, and have led to improved processing protocols. Research into the theory and measurement of bond length distortions in strained semiconductor alloys is leading to a unifying picture of macroscopic elasticity and the microscopic distortions which arise from alloying and pseudomorphic strain.

Publications:

G. Beaucage, J. H. Aubert, S. Rane, K. Schwartz, D. W. Schaefer, G. Wignall, G. Long and D. Fischer, "Morphology of Polyethylene/carbon black composites using SAXS," Appl. Phys. Lett., in press (1998).

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H. Kerch, G. G. Long, S. Krueger, A. J. Allen, R. Gerhardt, and F. Cossandey, "Characterization of porosity over many length scales: application to colloidal gels," J. Mat. Res., in press (1998).

J. J. Thomas, H. M. Jennings, and A. J. Allen, "The surface area of cement paste as measured by neutron scattering - evidence for two C-S-H morphologies," Cement and Concrete Research, in press (1998).

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R. Thomson, L. E. Levine, and G. G. Long, "Small-angle scattering by dislocations," Acta Cryst. A, in press (1998).

J. C. Woicik, J. O. Cross, C. E. Bouldin, B. Ravel, J. G. Pellegrino, B. Steiner, S. G. Bompadre, L. B. Sorenson, K. E. Miyano and J. P. Kirkland, "Diffraction anomalous fine structure study of strained $Ga_{1-x}In_xAs$ on GaAs (001), *Phys. Rev.* **B58**, Rapid Communications (1998) R4215 - R4218.

J. C. Woicik, J. G. Pellegrino, B. Steiner, K. E. Miyano, S. G. Bompadre, L. B. Sorenson, T. L. Lee, and S. Khalid, "Bond length distortions in strained semiconductors," *Phys. Rev. Lett.* **79** (1997) 5026- 5029.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Damage in Sapphire

Principal Investigators: David Black and Robert Polvani (Automated Production Tech. Div., MEL)

Technical Objectives:

The technical objectives of this project are: 1) to develop diagnostic tools to detect surface and subsurface damage, residual stresses and other crystallographic defects in single crystal sapphire; 2) to use these techniques to observe the effects of growth, fabrication processes, or other property enhancing procedures; and, 3) to correlate the observations to both design predictions and observed tests.

Technical Description:

The superior optical, chemical and thermal properties of sapphire, make large single-crystals the material of choice for IR seeker windows and domes for anti-ballistic missiles. In service, the crystals experience thermal shocking from the large thermal stresses, which can lead to failure. Factors affecting the in-service reliability of these components include surface flaws, residual stresses from the growth process and crystallographic orientation of the components. To produce windows and domes at the lowest cost and highest reliability, processing flaws, both surface and subsurface, must be identified and minimized. Residual stresses from growth or other processing procedures must also be identified and minimized, and lastly, the thermal structural models used for the design of these components must be verified.

The technical objectives of this project are being met with a series of experiments measuring the fracture strength of modulus of rupture (MOR) bars or the survival time of production domes under simulated flight conditions. The bars are part of the Sapphire Statistical Characterization and Risk Reduction (SSCARR) program. This is an inter-service (Air Force, Army and Navy) program meeting two needs: developing an engineering database for design engineers and exploring new methods to improve the bulk strength of sapphire. The set of MOR bars combines the effects of crystal growth method, sample fabrication technique, crystallographic orientation, and post-fabrication processing. It represents all combinations currently used in antiballistic missile programs. Here, the effects of crystallographic orientation, surface finish, growth method and surface coatings on the reliability of actual production domes is being evaluated using a supersonic wind tunnel. The Johns Hopkins Applied Physics Laboratory wind tunnel is being used to duplicate "mission" conditions. X-ray topography, surface finish and optical microscopy (including Nomarski, transmitted polarized light, and low magnification oblique lighting) are all used before and after

testing to evaluate the relative importance of each factor on reliability. Post mortem examination of failed components are providing a way to pinpoint the causes of failure.

External Collaborations:

Prof. Peter Lagerloff of Case Western Reserve University is involved in the preparation of samples and in the interpretation of data. Fred Schmid, Maynard Smith and Mark Felt of Crystal Systems Inc. grow high quality sapphire, supply samples with specific surface preparation and perform thermal treatments. Dr. Dan Harris of the Naval Air Warfare Center supplies samples and collaborates in the interpretation of data. Fracture data are supplied by the University of Dayton Research Institute. Mr. Kelly Frazer of the Johns Hopkins University Applied Physics Lab has technical responsible for the wind tunnel survivability tests and Dr. Jim Gotlieb from Ratheon Missile Systems Company has project responsibility for the thermomechanical analysis of the domes.

Accomplishments:

X-ray topography has been used successfully to characterize the curved surface of domes in a variety of diffraction conditions. Specific diffraction conditions have been identified to emphasize surface structures in the highest stress regions of the domes. It was found that the application of a surface coating does not change the long-range strain field.

Publications:

David Black, "X-ray diffraction imaging of sapphire for windows and domes," Proceedings of the 7th DoD Electromagnetic Windows Symposium, May 5-7, 1998 APL, Laurel, MD.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Development of an Instrument for X-Ray Microtomography

Principal Investigator: Richard Spal

Technical Objective:

The technical objective is to develop an instrument for performing microtomography of ceramics and other materials, at spatial resolutions down to 1 μm, using the NIST/UNICAT undulator beamline at the APS. The spatial resolution and field of view will be adjustable by a factor of about 4, with the field increasing from 250 μm to 1000 μm as the resolution varies from 1 μm to 4 μm. Data acquisition will take less than 1 h, for objects smaller than the field of view. The instrument will operate with monochromatic radiation ranging from 8 keV to 40 keV. Finally, the instrument will be portable, since it must be stored outside the experimental hutch when not in use.

Technical Description:

The instrument consists of three stages-the aperture, object, and image stages- which are assembled on an optical table and receive the incident beam in the order listed. The table rests on three rigid kinematic supports, and is transported by an elevating carriage which fits between the supports. The aperture stage has orthogonal slits, a shutter, and an ion chamber.

The object stage has a rotator to turn the object about the primary axis, four translators to center the object on the primary axis and in the beam, and two rotators to orient the primary axis. During a tomographic scan, only the rotator which turns the object about the primary axis, and two translators which center the object on the primary axis, are used. Consequently, these three positioners have the highest precision: the rotator has radial and axial runout below 0.1 μm, which is achieved with a rotary air bearing; and the translators have repeatability of 0.05 μm, which is achieved with 0.05 μm resolution encoders and servo control.

The image stage has an asymmetric Bragg diffraction microscope (ABDM), and translators to position the ABDM along three axes. The ABDM uses asymmetric Bragg diffraction from a pair of flat silicon crystals to magnify the radiographic image of the object by an adjustable factor, ranging from 10 to 40 as the spatial resolution varies from 4 μm to 1 μm. The magnified x-ray image is converted by a single crystal x-ray scintillator to a visible image, which is focused by a lens without further magnification onto a 1 x 1 cm^2 charged coupled device (CCD) detector with 20 μm x 20 μm pixels. This microscope is an improved version of one which was routinely used to perform microradiography at about 1 μm resolution on the NIST beamline X23A3 at the NSLS.

The optics are different from those in the conventional x-ray tomographic microscope used at many synchrotron radiation facilities. In the conventional instrument, the radiographic image is converted, without prior magnification, by a scintillator to a visible image, which is then magnified by a lens. The advantage of magnifying before the scintillator is that the scintillator can be made much thicker, giving it much higher detection efficiency, without degrading the spatial resolution.

Finally, vibrational stability is a major consideration in the design and selection of all positioning and structural elements of this instrument, since relative vibration between the object and image stages must be kept substantially below 1 μm.

External Collaborations:

Collaborators in this work include Haydn Chen and T. C. Chiang, University of Illinois, Gene Ice and Ben Larson, Oak Ridge National Laboratory, and Robert Broach, UOP Corporation.

Planned Outcomes:

An instrument for performing microtomography will be developed, thereby creating a versatile, state-of-the-art instrument which will be applied nondestructively to study materials having inhomogeneities on a scale of 1 μm and greater.

Accomplishments:

Two key features have been implemented for the first time in an instrument for microtomography. The first feature is an air bearing on the primary rotation axis, which assures that runout will not be a significant source of error. Solid bearings generally have runouts in excess of 1 μm, which cannot be corrected easily. The second feature is an ABDM, which enables use of a scintillator with much higher detection efficiency, as mentioned above. (It should be noted that some instruments for microtomography already use a one-dimensional ABDM, which provides magnification in one direction only, but none uses a two-dimensional ABDM.)

The ABDM has been improved significantly compared to its predecessor at the NSLS. For example, the earlier instrument converted x-rays directly to electrical charge in the CCD, rather than indirectly *via* visible photons emitted by an x-ray scintillator. The incorporation of the scintillator greatly increases the x-ray detection efficiency, and eliminates radiation damage to the CCD. Finally, procurement of the mechanical components of the instrument is nearly complete.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: NIST/Dow Soft X-ray Materials Characterization Facility at NSLS

Principal Investigator: Daniel A. Fischer

Technical Objective:

The objective is to develop a unique world class facility for ultrasoft x-ray absorption spectroscopy of diverse materials important to NIST and our industrial partners.

Technical Description:

The U7A materials science end station is a materials characterization facility with unprecedented power, complete with instrumentation and analysis capabilities. The key feature of the end station is that it enables non-ultrahigh vacuum ultrasoft x-ray materials characterization that may be applied to studies of catalysis, biomaterials, polymer science, data storage applications, high-Tc superconductivity, and tribology.

External Collaborations:

Collaborators in this work include Ben DeKoven (Dow), Sarah Sambasivan (Dow/NSLS), Timm Richardson (Dow), and Alex Kuperman (Dow).

Planned Outcomes:

Measurement facilities and procedures will be established and maintained to conduct materials characterizations using ultrasoft x-ray radiation.

Accomplishments:

This year, the final major construction phase of the Dow / NIST soft x- ray materials characterization facility was completed.To accomplish this, the existing facility had to be completely dismantled and reconstructed. A refocusing mirror, which delivers a sub-millimeter spot size and also enables a one-minute turnaround between the surface-science and the materials-science end stations, was installed. The sample preparation and load-lock chamber was installed. And the final critical element, the new wavelength-dispersive detection system, was installed and commissioned. Nearly background free carbon NEXAFS spectra can now be recorded in typical samples in under one-half hour.

It is now possible to obtain previously inaccessible *in situ* data on polymers and catalysts. Ultrasoft x-ray measurements and analysis are now routinely used in polymer science, catalysis, high-Tc superconductivity, and, most recently, tribology. (See the Dental and Medical Materials program and also the Magnetic Materials program in this report.)

Publications:

J. Genzer, E. Sivaniah, E. Kramer, J. Wang, H. Korner, X. Maoliang, S. Yang, C. Ober, M. Chaudhury, B. DeKoven, R. Bubeck, D. Fischer, S. Sambasivan, "Surfaces of semi-fluorinated block copolymers using NEXAFS," in *Applications of Synchrotron Radiation Techniques to Materials Science IV*, S. M. Mini; D. L. Perry; S. R. Stock; L. J. Terminello Eds., Materials Research Society Symposium Proceedings, Vol. **524** (Materials Research Society: Pittsburgh, 1998), pp. 365-370.

PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Semiconductor Materials Evaluation

Principal Investigator: Joseph C. Woicik

Technical Objective:

The technical objective is to develop measurement techniques utilizing synchrotron radiation for the characterization of novel semiconductor device structures fabricated by advanced growth techniques such as molecular beam epitaxy (MBE) and chemical vapor deposition (CVD). Validation of these techniques is achieved by means of comparisons between ultra-high resolution measurements and theoretical predictions of atomic and electronic structures.

Technical Description:

When a macroscopic body is acted upon by external forces, its reversible deformations are accurately described by the theory of elasticity. Implicit to the theory of elasticity are the microscopic, atomic-scale structural distortions that truly govern the macroscopic behavior of the body. This year, the problem of determining bond-length strain in strained semiconductor thin-alloy films was solved using a combination of x-ray techniques at the NSLS.

The problem of bond length determination in these strained materials also addresses the fundamental issue linking microscopic (bond length and bond angle) distortions with the macroscopic elastic behavior of a body. The importance of this work should become evident in future calculations of the electronic properties of layered structures.To solve the problem, the most precise (standard uncertainty of 0.003 Å) bond length measurements to date were made. The measurements were performed on extremely thin alloy films, where these EXAFS measurements rival any of the highest quality transmission measurements that have been performed on bulk samples.

In addition to solving the bond length problem experimentally, a theoretical framework for the calculation of the geometric structure of strained semiconductor alloys was developed based on a random cluster, statistical mechanics approach. The model was tested by performing an extremely difficult diffraction anomalous fine-structure (DAFS) experiment on the same sample studied by means of EXAFS. DAFS is the only method capable of measuring the Ga-As bond length in the buried InGaAs alloy (which is grown on GaAs).

External Collaborations:

J.G. Pellegrino (EEEL, NIST) provided the III-V strained semiconductor alloys grown coherently on lattice-mismatched substrates by MBE. C.A. King (Lucent Technologies, Bell Laboratories) has grown both strained and relaxed IV-IV materials by CVD. James Gupta (Simon Fraser University) has also provided III-V strained layer material by CVD. T. Moustakas (Boston University) has provided ordered AlGaN thin-alloy films. Collaboration has begun with P. Pianetta (Stanford University) on coupled beam experiments of valence charge density.

Planned Outcomes:

A unifying description of atomic structure and elastic response in strained-layer ordered and disordered semiconductor alloy heterostructures will be established. An additional planned outcome is the development of a new and direct technique for the investigation of bonding in crystalline materials.

Accomplishments:

The problem of local geometric structure in strained-layer, quasi-bulk semiconductor thin-alloy films has been solved. The results from ultra-high resolution extended x-ray absorption fine structure (EXAFS) data and diffraction anomalous fine structure (DAFS) data measuring the bond lengths within well characterized strained alloys are found to be in agreement with theoretical valence-force field calculations.

Preliminary data utilizing two coupled x-ray beams has shown that direct measurements of bond polarity in crystalline materials can be made, overcoming the problems associated with scattering measurements of charge density.

Publications:

J.C. Woicik, J.G. Pellegrino, B. Steiner, K.E. Miyano, S.G. Bompadre, L.B. Sorensen, T.-L. Lee, and S. Khalid, "Bond length distortions in strained semiconductor alloys," *Phys. Rev. Lett.* **79**, 5026 (1997).

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PROGRAM TITLE: Synchrotron Radiation Characterization

PROJECT TITLE: Studies of Regularity in Optoelectronic Materials

Principal Investigator: Bruce Steiner

Technical Objective:

The scientific objective of this project is insight into crystal regularity, which provides an essential cornerstone for the design and effective commercial realization of novel single crystals for the next generation of photonic and electronic devices in the US. This objective is achieved through high resolution synchrotron radiation diffraction imaging and its interpretation.

Specific current technical target areas include advanced radiation detectors, crystals for quasi phase-matched laser frequency doublers, and higher yield in the production of guided wave modulators for enhanced position sensors and maximum capacity communications. Applications for these devices are: increased simplicity and reliability in monitoring nuclear technology, short wavelength lasers for high capacity information storage and rapid communications, and increased sensitivity in orientation during travel and innovative approaches to information processing. Priorities are established and research is carried out in collaboration with colleagues in industry, governmental laboratories and mission agencies, and universities.

Technical Description:

These technical objectives are achieved through the exploitation of special high sensitivity crystal characterization facilities and specialized expertise in crystalline irregularity associated with advanced crystals. One of the NIST MSEL beamlines at the National Synchrotron Light Source at Brookhaven National Laboratory, Beamline X23A3, is used in conjunction with *in situ* laser optical fields. High resolution diffraction imaging, guided by the experimental and interpretive expertise established through this activity, leads to the identification of crystalline irregularity, the study of its influence on device performance, the determination of its genesis, and the achievement of its control through materials and device processing. The resulting insight provides a reliable basis for device design, performance optimization, and economical production of novel devices for the next generation of information processing technology

Activity currently includes: lithium niobate frequency doublers; guided wave modulators for fiber optic gyroscopes for increasingly precise position sensors; wafer bonded systems for flat panel displays; laser materials for blue lasers; and mercuric iodide grown in microgravity and on the ground for optimized low noise, room temperature, high energy radiation detectors.

External Collaborations:

Current work involves: William Burns of the Naval Research Laboratory, with whom we are working on the scientific basis for frequency doubler technology; Peter Bordui and Dieter Jundt of Crystal Technology, Inc., which produces lithium niobate for these devices and for optoelectronic guided wave switches; Norman Sanford, Richard Mirin, and Andrew Aust of the Optoelectronics Division of the NIST Electronics and Electrical Engineering Laboratory, which produces and characterizes similar devices; Joseph Pellegrino of the Semiconductor Electronics Division, also of the NIST Electronics and Electrical Engineering Laboratory, which produces and studies innovative III-V materials and devices; and Lodewijk van den Berg of Constellation Technology, Inc. Dr van den Berg is developing mercuric iodide detectors for high energy radiation as a follow up to a Department of Energy program in nuclear sensors and NASA microgravity crystal growth programs. His collaboration is valuable not only because of his commercial perspective but also because of his roll as Principal Investigator for both space flights involved and his participation as the scientist who grew the first successful crystals himself in microgravity as mission specialist on board Spacelab III.

Planned Outcomes:

A primary target is modification of the lithium niobate defect structure for enhanced high frequency capacity for frequency doublers. The fabrication of high frequency doublers for lasers supports greater US competitiveness in the production of high frequency optical sources for increased capacity information processing. Closely related targets are useful understanding of the evolution of strain during growth of lithium niobate crystals for fiber optic position sensors as well as for wavelength division multiplexing supporting enhanced capacity in fiber optic communications, and effective reduction in the removal of wafer material in cutting and polishing in order to achieve increased flatness for advanced photonics. Growers of highly uniform lithium niobate single crystals will be able to make knowledgeable, economical trade-offs between crystal perfection and performance. One result is that the establishment of an elaborate subgrain structure can now be prevented when it is cost-effective to do so.

A new target is an understanding of defect structure in wafer bonded systems, which promise to provide inexpensive and highly efficient electrooptic devices for flat panel displays, which appear to be approaching wide commercial application.

Another new target is the development of efficient, durable blue laser materials for high density information storage and transmission systems. This technology also is also approaching commercial realization, with keen competition between Japan and the US.

A longer term target is insight into the crystallographic sources of the enhanced performance of low noise, room temperature, high energy radiation detectors made from mercuric iodide crystals grown in microgravity and its application to superior mercuric iodide grown on the ground.

Accomplishments:

Two principal sources of the high frequency roll-off in lithium niobate frequency doublers have been identified. One is a set of widely dispersed mixed dislocations. The second is a subgrain structure whose boundaries interfere with the establishment of the desired domains.

The unnecessary removal of material in the polishing of lithium niobate has been pinpointed, leading to the manufacture of flatter lithium niobate devices with enhanced performance.

The crystallographic origins of the enhanced performance of low-noise, room-temperature, high-energy radiation detectors made from mercuric iodide have been identified and this understanding utilized in the manufacture of room temperature detectors with enhanced performance.

Publications:

J. C. Woicik, J. G. Pellegrino, B. Steiner, K. E. Miyano, S.G. Bompadre, L B. Sorensen, T.-L. Lee, and S. Khalid, *"Bond-Length Distortions in Strained Semiconductor Alloys,* Phys. Rev. Lett. **79**, 5026-5029 (1997)

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Bruce Steiner, Lodewijk van den Berg, and Uri Laor, "Gravitational Effects on Mercuric Iodide Crystal Growth," MRS Symp. (Mat. Space - Sci., Tech., and Expl). (1998)

OTHER

Several important projects in the Ceramics Division are unique and are not constituent parts of "Programs." These projects are highly visible and have significant broad impact in several application areas but generally involve a commitment of personnel and resources less than that considered to be a program. The Ceramics Division relies on these projects for enhanced technology transfer and for more effective delivery of the results of the research programs to the technical community.

PROGRAM TITLE: Other

PROJECT TITLE: Characterization of Cements

Principal Investigators: Andrew J. Allen

Technical Objectives:

The objectives of this research is to characterize microstructure evolution during hydration in cements, to determine what aspects of the microstructure relate most directly to performance, to characterize microstructure degradation due to environmental effects, and to probe the effects of additions of silica fume, fly ash, and other additives that may lead to superior performance.

Technical Description:

This project makes use of small-angle neutron scattering (SANS) and ultra-small-angle x-ray scattering (USAXS) to characterize microstructural evolution during the hydration of cements, as a function of environmental effects and additives, as it affects highway infrastructural concretes. While previously the program has focussed on the effects on cement hydration of silica fume (SF), the studies have now moved on to the effects of coal fly ash (CFA), a major coal combustion by-product resulting from electrical power generation. Like SF, CFA is increasingly being used as a relatively inexpensive additive in cement and concrete, intended to enhance cement and concrete durability. Two CFA's are currently being studied using USAXS, from which the fly ash particle size distributions have been determined. Subtle differences are observed throughout the size range between these two basic types of CFA: F and C. SANS studies are currently underway to determine the different effects of these distributions on cement microstructure development during hydration. Our fundamental SANS studies of cement hydration are beginning to explore the formation of different types of the main strength-developing calcium-silicate-hydrate (C-S-H) phase as hydration proceeds.

External Collaborations:

R.A. Livingston, Federal Highway Administration, McLean monitors this program and is involved in interpretation of the SANS and USAXS measurements. J. Thomas and H.M. Jennings, Northwestern University, collaborate with the Ceramics Division on surface area and C-S-H gel characterization in hydrating cements utilizing SANS as the primary technique.

Planned Outcome:

These studies will enable a quantitative assessment of how the microstructures of hydrating cement systems can be controlled, by the hydration conditions and by the use of cement additives. The

studies have already quantified the relationship between differences in silica fume morphology and the variable effectiveness of silica fume additives in forming cements and concretes of improved strength and durability. Present work is focussed on similar objectives for coal fly ash additives.

Accomplishments:

A combined SANS and USAXS study is underway to quantify the microstructural effects of CFA additives on cement microstructure development during hydration. Coal fly ash is a finely divided air-borne coal combustion by-product, collected by electrostatic precipitators inserted into the flue gases of coal fired electrical utilities. Like SF, CFA is mainly comprised of silica particles although these are not as fine as in SF, and there is usually a large fraction of other material such as CaO present, particularly in CFA type C. Like SF, CFA additives react with the cement during hydration and can improve the strength and durability. Important differences are that the effects of CFA occur over more extended times and there is a greater variability associated with the wider range of CFA phase composition. Preliminary USAXS studies on the CFA powders have revealed subtle differences between the particle size distributions of the two CFA types with type C having a bimodal size distribution with mean particle sizes of 0.2 μm and 0.8 μm. Type F has a broad continuous size distribution with a mean at around 0.5 μm. Further measurements on slurry suspensions are required to confirm these results.

CFA additives are used in cements in higher proportions than are SF additives. A 10 % - 20 % replacement by mass is typical, compared to 5 % - 10 % for SF. Differences in cements prepared using types C and F are manifest even at the sample mixing stage. More than a dozen samples have been prepared for SANS studies, now underway, that are designed to characterize the cement microstructure evolution over time, as a function of type and amount of CFA added together with the water-to-solids ratio in the cement mix. Our semi-fractal microstructure model is being used to quantify the microstructural development and relate this both to known cement and concrete properties and to the CFA particle morphologies determined by the USAXS studies above.

Our studies of the microstructural effects of SF and CFA in infrastructural cements and concretes have become more focussed on how these additives affect the fundamentals of C-S-H gel formation. This has brought this work closer to our fundamental SANS studies concerning a possible coexistence of two different C-S-H morphologies in hydrating cement systems. It was reported previously that a series of experiments, exploring the effects of water-to-cement ratio, temperature, age, and other hydration conditions, had established that the high surface-area form of C-S-H adjusts its long-range morphology to fit the available space, and that this is the main agent binding the cement grains together. While this certainly seems to hold in the case of a pure Portland cement, it is now becoming clear that the addition of SF or CFA additives can also adjust this long-range morphology and perhaps increase the amount of C-S-H gel in the high surface area form. The addition of the well known hydration accelerator, calcium hydroxide, appears to have a similar effect, while this is not the case for the other accepted method of accelerating cement hydration:

increasing the temperature. It remains to determine whether such changes in the high surface-area form of C-S-H are reflected in corresponding changes in the dense C-S-H form, believed to dominate the hydration reactions after the first 24 h. Certainly, these results are revealing why the development of cement and concrete properties can frequently not be easily related to the degree of hydration, as measured by the heat output of the hydration reactions.

Publications:

J.J. Thomas, H.M. Jennings and A.J. Allen; "Determination of the Neutron Scattering Contrast of Hydrated Portland Cement Paste using H_2O/D_2O Exchange", Adv. Cem. Based Mater., **7** 119-122 (1998).

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A.J. Allen and R.A. Livingston; "The Relationship Between Differences in Silica Fume Additives and the Fine Scale Microstructural Evolution in Cement-Based Materials", Adv. Cem. Based Mater., **8** 118-131 (1998).

PROGRAM TITLE: Other

PROJECT TITLE: Evaluated Materials Property Data

Principal Investigator: Ronald G. Munro

Technical Objective:

The objective of this project is to develop and promote the scientific basis for data evaluation and its practical application to materials property databases to enhance the quality and reliability of materials property data for advanced ceramics.

Technical Description:

The most persistent concern regarding the use of materials property data in industry is the reliability of the data. The lack of reliable data can result in significant losses of resources and untimely production failures. However, few design engineers and materials researchers have the resources to explore the full depth and range of publications that have been issued on a given material, and even fewer have the opportunity to assess the relevant reports fully. Consequently, there is a considerable need for the establishment of systems of evaluated property data.

The process by which data become acknowledged as reliable is often termed data evaluation. In this project, there are four distinguishable stages of data evaluation: (I) data collection from selected sources, (II) application of basic evaluation criteria, (III) relational analysis, and (IV) modeling. Useful results are derived from each stage of the evaluation process.

Stages III and IV are considered advanced data evaluation stages. In these stages, the view taken in the present project is that a material may be fully represented by its collection of measurable properties and characteristics. Experimentally, few materials are ever studied in this context. Commonly, one property measurement is made in isolation from other property measurements, and each study pertains only to the specific batch of material used in the study. In the present project, physical, thermal, and mechanical property data are compiled for one nominal material specification. Subsequently, the collection is analyzed with respect to chemical composition, density, grain size, and other characteristics as needed. When sufficient constraints on these characteristics have been identified such that the property values are observed to be consistently reproducible in independent studies, then the corresponding subset of data is refined into a selfconsistent collection of property values. Theoretical and empirical property relations and statistical correlations are used as needed and warranted by the refinement.

Data assessed by each of the four stages of evaluation are collected in evaluated databases and made publicly available *via* both the NIST Standard Reference Data Program and the Ceramics Division's website. A data quality indicator, called the data evaluation level, is provided with each data set to indicate the extent of assessment that has been applied to the data.

Planned Outcomes:

Data evaluation methodologies, including the use of data quality indicators and specific assessment procedures, will be established and applied to the development and maintenance of the Structural Ceramics Database, the High Temperature Superconductors Database, the Ceramics Coatings Database, and the NIST Property Data Summaries.

Accomplishments:

The advanced data evaluation methodology has been applied to sintered α-SiC. Sintered α-SiC has evolved as a major structural ceramic with applications that include heat exchangers for high temperature and aggressive environments, seals, bearings, and wear resistant components. It was found that a selfconsistent set of property values could be developed for this material when the density was approximately (98±1) % of the density of single crystal SiC(6H) with a mean grain size of (6±2) μm, and the composition of the sintered material included mass fractions of boron and free carbon of (0.4±0.1) % and (0.5±0.1) % respectively.

An extensive collection of fracture toughness data for brittle materials has been compiled, in collaboration with S. W. Freiman and T. L. Baker. The collection included data for 115 materials. An analysis of the distribution of observed values in this collection showed that the fracture toughness of thermodynamically stable brittle materials was in the range from 1 $MPa \cdot m^{1/2}$ to 8 $MPa \cdot m^{1/2}$.

Version 3 of the Structural Ceramics Database gained final approval from the NIST Standard Reference Data Program (SRDP) and became available from the SRDP in pc-format using the pc-interface developed in collaboration with E. F. Begley. Version 3 extended the scope of materials covered by the SCD to include borides, carbides, nitrides, oxides, and oxynitrides.

In collaboration with E. F. Begley of the Ceramics Division, the High Temperature Superconductors Database and the Structural Ceramics Database have been made available on the World Wide Web. These databases, known on the web, respectively, as WebHTS and WebSCD, can be accessed *via* the NIST Ceramics Division's website, http://www.ceramics.nist.gov/, under the heading Ceramics WebBook.

Publications:

R. G. Munro and H. Chen, "Data Evaluation Methodology for High Temperature Superconductors," ASTM STP 1311, pp. 198-210 (1997).

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R. G. Munro, S. W. Freiman, and T. L. Baker, *Fracture Toughness Data for Brittle Materials*, NISTIR 6153 (National Institute of Standards and Technology, 1998).

R. G. Munro and E. F. Begley, SRD Database Number 62: *High Temperature Superconductors, Version 2*, NIST Standard Reference Materials Program (1997).

R. G. Munro and E. F. Begley, SRD Database Number 30: *Structural Ceramics, Version 3*, NIST Standard Reference Materials Program (1998).

R. G. Munro, NIST Property Data Summaries for Advanced Materials: *Al_2O_3*, 1998, NIST Ceramics WebBook, http://www.ceramics.nist.gov.

R. G. Munro, NIST Property Data Summaries for Advanced Materials: *SiC*, 1998, NIST Ceramics WebBook, http://www.ceramics.nist.gov.

R. G. Munro, NIST Property Data Summaries for Advanced Materials: *Fracture Data for Brittle Materials*, 1998, NIST Ceramics WebBook, http://www.ceramics.nist.gov.

PROGRAM TITLE: Other

PROJECT TITLE: Development of the Ceramics WebBook

Principal Investigator: Edwin F. Begley

Technical Objective:

The objective of this project is to develop the NIST Ceramics WebBook.

Technical Description:

The international success of the World Wide Web precipitated the vision of the NIST Ceramics WebBook to provide industry and the general public with efficient and ready access to Ceramics Division reference databases, topical data sets, data guides and advisories, and tools as well as other resources related to advanced ceramic materials.

External Collaborations:

During fiscal year 1996, the Systems Integration for Manufacturing Applications Program (SIMA) funded initial development of WebHTS, the World Wide Web version of the NIST High Temperature Superconducting (HTS) Materials Database. This task was designed to address on-line access to standard reference data which is a key SIMA program area for testbeds and technology transfer. In fiscal year 1997, renewed SIMA funding was used to complete WebHTS and to expand the testbed to include demonstrations of electronic collaboration and, also, the transfer of different types of technical information. In fiscal year 1998, SIMA funding was used to port the NIST Structural Ceramics Database (WebSCD) to the World Wide Web and to initiate the development of the NIST Ceramics WebBook. The Characterization of Fracture Origins in Advanced Ceramic Materials WebBook site was developed in collaboration with the United States Army Research Laboratory.

Planned Outcome:

The outcome of this project is the development of a World Wide Web site that will serve as an effective means of disseminating Ceramics Division reference databases, topical data sets, data guides and advisories, and tools as well as other resources related to advanced ceramic materials.

Accomplishments:

In 1996, the Property Data Summaries collection was placed on the Web and is continually updated. In 1997, the NIST High Temperature Superconducting Materials Database was ported to the Web (WebHTS). In 1998, the NIST Ceramics WebBook was added to the Ceramics Division website and the NIST Structural Ceramics Database was ported to the Web (WebSCD).

In addition, in 1998 the Guide to Materials Data Centers and Sources was added to the Ceramics WebBook as well as a website on the Characterization of Fracture Origins in Advanced Ceramic Materials and downloadable software entitled the "VAMAS Classification System for Advanced Technical Ceramics Evaluation/Demonstration Software." Links to external (non-NIST) tools and data collections were also added to the WebBook in 1998.

Publications:

E. F. Begley, Web site of the NIST Ceramics Division, 1997, http://www.ceramics.nist.gov/.

Web site of the NIST High Temperature Superconducting Materials Database, E.F. Begley and R.G. Munro, 1997, WebHTS at http://www.ceramics.nist.gov/srd/hts/htsquery.htm.

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E.F. Begley and R.G. Munro, Web site of the NIST Structural Ceramics Database, 1998, WebSCD at http://www.ceramics.nist.gov/srd/scd/scdquery.htm.

R. G. Munro, E. F. Begley,Web site ofthe NIST Property Data Summaries for Advanced Materials, http://www.ceramics.nist.gov/srd/summary/advmatdb.htm.

PROGRAM TITLE: Other

PROJECT TITLE: SRMs for Powder Diffraction

Principal Investigators: James P. Cline, Richard D. Deslattes and Jean-Louis Staudenmann (Physics Laboratory), Brian H. Toby (Reactor Radiation Division)

Technical Objective:

The objective of this project is to develop NIST Standard Reference Materials (SRMs) to enhance the measurement capabilities of the materials science community.

Technical Description:

NIST powder diffraction SRMs are developed for the determination of: 1) the d-spacing or line position, 2) line intensity as a function of position, or instrument sensitivity, and 3) instrumental and sample contributions to the shape of reflection profiles. Additional powder diffraction SRMs are designed for quantitative analysis for use with the internal standard method.

We are presently pursuing a new generation of line position SRMs which will be certified *via* a robust linkage to the iodine stabilized HeNe laser length standard. This project has involved the construction of a diffractometer capable of measurement accuracy to the parts per million range. The machine has several unique features: a dual mirror optic that results in a parallel incident beam of high flux from a laboratory source, and an encoded goniometer capable of achieving sub-arcsecond accuracy, and symmetric scanning about the zero angle. These features permit measurements, which use the emission spectra of copper, to be free from penetration and centration errors of the sample, and from zero errors of the goniometer. The silicon powder to be used for the SRM is being prepared from a dedicated production run of intrinsic material grown by the float zone method. The feedstock has been prepared by jet milling to produce a powder with a narrow particle size distribution with a mean of approximately 3.5 μm.

The observed diffraction profile from the diffractometer consists of a sample profile convolved with an instrument profile and with noise superimposed. The sample profile includes the broadening due to crystallite size and micro-strain effects within the sample. Although there exist several methods of determining the sample profile they often require specific assumptions concerning the functional form of the sample profiles; otherwise, the solutions may be ill-conditioned. The approach which has been developed to solve this problem is to apply the Maximum Entropy method (MaxEnt) which incorporates *a priori* information about the instrument profile and noise distribution as constraints and determines the solution which maximizes the entropy with respect to these constraints. Our research is concentrating on

developing a generalized MaxEnt/Bayesian method which could be applied to deconvolving and separating overlapped profile peaks and which could be adopted for crystallite size and micro-strain analysis.

The instrumental contribution to observed line profile shape from x-ray diffraction equipment can be characterized with SRM 660 (LaB_6). This material was selected through an International Centre for Diffraction Data sponsored round robin which found that it displayed minimal peak broadening due to crystallite size and micro-strain effects. Refinements of the SRM's evenly spaced, high intensity diffraction lines yield precise values for parameters of the selected profile shape function. Due to its certified lattice parameters, SRM 660 can also be used for determining instrumental parameters through a Rietveld refinement. SRM 660a, the renewal of SRM 660, is under development. An improved feedstock of LaB_6 has be prepared which displays significantly less micro-strain broadening than does SRM 660. SRM 660a will be certified for lattice parameter with the aforementioned high resolution, parallel beam diffractometer. Also under development is an SRM which will display the effects of particle size induced profile broadening

SRMs are also being characterized for use in quantitative analysis by powder diffraction methods of special interest is the effect of the disordered surface layer, caused by relaxation and unsatisfied bonds, that must accompany any boundary of a crystalline material. Such a boundary layer will not diffract in a manner analogous to the bulk and can be considered amorphous. In a finely divided solid, a layer of 1 or 2 crystallographic units in thickness can amount to several percent of the total mass. To perform an accurate quantitative analysis which includes the amorphous content, a standard of known phase purity must be used. Thus, a major focus of the work in this area has been the development of a measurement and certification method for the amorphous content of SRM 676, a non-orienting alumina powder which is presently certified with respect to lattice parameters and eight relative intensity values.

External Collaborations:

Robert B. Von Dreele (Los Alamos National Laboratory), Walter Kalceff and Nicholas Armstrong (University of Technology, Sydney) collaborate this project.

Planned Outcomes:

Certification of a new generation of line position SRMs with roughly an order of magnitude improvement in certainty of the certified lattice parameters will be completed with the new diffration equipment The MaxEnt/Baysian approach to profile deconvolution and analysis of particle size/micro-strain induced profile broadening will be established. The certification of amorphous content in SRM 676 will be measured to an improved level of accuracy.

Accomplishments:

A powder diffractometer capable of lattice parameter measurements to the parts per million range has been constructed.

The amorphous content of SRM 676, alumina powder, has been determined to within a few tenths of a percent.

The experimental approach is based on the comparison of the phase abundance of two phase mixtures determined from the preparation procedure using an analytical balance, which includes the amorphous component, to that determined from the diffraction data, which does not. Specimens consisted of 50-50 mixtures of SRM 676 and silicon powder, the latter material having been obtained from crushed and jet milled single crystal, electronic grade boules. This microstructure allowed for the assumption that all amorphous material in the silicon powder was confined to a surface layer on the particles, and that the thickness of the layer was constant with respect to particle size. Thus, by systematically varying the surface area of the silicon powder, we could model its effect on the data. However, prerequisite to the success of this method was an unbiased measurement method. Potential for bias was judged from the plausibility of the refined results obtained from a number of powder diffraction methods. Data were collected *via* time-of-flight, TOF, and constant wavelength, CW, neutron powder diffraction, and synchrotron and conventional x-ray powder diffraction. Analysis of the refinements indicated that the TOF data were the least biased, and thus the amorphous content of the alumina was credibly determined.

SRM 674a consists of a set of five powders: α-Al_2O_3, ZnO, TiO_2 (rutile), Cr_2O_3, and CeO_2, which range in x-ray mass attenuation coefficients from 126 cm^{-1} to 2203 cm^{-1} (Cu Kα). The materials available with this SRM permit the minimization of absorption contrast between the standard and the specimen. SRMs 1878a (α-quartz) and 1879a (cristobalite) were certified with respect to amorphous content for analysis of silica containing materials in accordance with health and safety regulations. Quantitative analysis of the silicon nitride system can be performed with SRM 656 which consists of two powders, one high in α content while the other is high in β. They are certified with respect to α /β ratio and amorphous content.

The Maximum Entropy Method has been applied to the deconvolution of the x-ray diffraction line profiles for the determination of sample induced profile broadening.

The effect of equipment optics on the observed position of profile maxima has been characterized and evaluated with a fundamental parameters approach.

*The Ceramics Division Staff E-mail addresses can be accessed using the **fname.lname.@nist.gov**, except as otherwise noted. (Example: stephen.freiman@nist.gov)*

Allen, Andrew J. 301/975-5982	• Small angle x-ray scattering • Ceramic microstructure analysis
Begley, Edwin F. 301/975-6118	• Database management methods • Engineering database structures • Digital video interactive technology
Black, David R. 301/975-5976	• Defect microstructure in diamond • Polycrystalline diffraction imaging • X-ray imaging of photonic materials
Blendell, John E. 301/975-5796	• Ceramic processing and clean-room processing • Sintering and diffusion controlled processes • Processing high-T_c ceramic superconductors • Activation chemical analysis
Bonnell, David W. 301/975-5755	• Computer automation • Molecular-beam mass spectrometry • Thermodynamic modeling • Laser/plasma sputtering
Bouldin, Charles E. 301/975-2046	• X-ray absorption spectroscopy • Diffraction anomalous fine structure • GeSi heterojunction bipolar transistors
Braun, Linda M. 301/975-5777	• Raman stress measurements • Ceramic matrix composites • Toughening mechanisms
Burdette, Harold E 301/975-5979	• X-ray optics • X-ray diffraction imaging • Crystal growth • Instrumentation
Burton, Benjamin P. 301/975-6043	• Calculated phase diagrams • Dielectric ceramics

Carpenter, Joseph A., Jr. 301/975-6397	• Functional ceramics applications • Technical assessments • Industrial liaisons
Cellarosi, Mario 301/975-6123	• Glass standards • Machining data
Chuang, Tze-Jer 301/975-5773	• Creep/creep rupture • Fracture mechanics • Finite-element modeling • Lifetime predictions
Clevinger, Mary A. 301/975-6109	• Phase diagrams for ceramists • Computerized data
Cline, James P. 301/975-5793	• Standard reference materials • High-temperature x-ray diffraction • Microstructural effects in x-ray diffraction • Rietveld refinement of x-ray diffraction data
Chan, Julia 301/975-6890	• Phase equilibria studies of dielectric oxides for wireless applications
Cockayne, Eric 301/975-4347	• First-principles computational studies of dielectric oxides
Cook, Lawrence P. 301/975-6114	• High-temperature chemistry • Phase equilibria
Dapkunas, Stanley J. 301/975-6119	• Structural ceramics applications • Technical assessments • Coatings
Feldman, Albert 301/975-5740	• Thermal properties • Modeling thermal wave propagation • Thin-film optical properties
Fischer, Daniel A. 516/344-5177 fischer@x23a3df.nsls.bnl.gov	• X-ray absorption fine structure • X-ray scattering • Surface science

Freiman, Stephen W. 301/975-6119	• Electronic ceramics • Mechanical properties
Fuller, Edwin, R., Jr. 301/975-5795	• Influence of microstructure on fracture • Toughening mechanisms • Microstructural modeling and simulation
Gates, Richard S. 301/975-3677	• Tribo-chemistry • Surface chemical properties of ceramics
Gonzalez, Eduardo 301/975-6102	• Ceramic Processing • Nano-scale sintering • Texture analysis
Hackley, Vincent A. 301/975-5790 vince.hackley@nist.gov	• Electrokinetic and electroactive measurement • Slurry rheology • Surface chemistry of powders.
Hastie, John W. 301/975-5754	• High-temperature chemistry • Phase equilibria thermochemistry • Molecular-beam mass spectrometry • Thin-film deposition • Vapor deposition process control and modeling
Haugan, Timothy 301/975-4954	• Applications of phase equilibria data to processing of high-temperature superconductors
Hockey, Bernard J. 301/975-5780	• Electron microscopy • High-temperature creep
Hsu, Stephen M. 301/975-6120	• Ceramic wear mechanisms • Engineered ceramic surfaces • Lubrication and machining of ceramics
Ives, Lewis K. 301/975-6013	• Wear of materials • Transmission electron microscopy • Machining of ceramics

Jahanmir, Said 301/975-3671	• Ceramic machining • Mechanisms of material removal • Mechanics of contacts • Effects of machining on mechanical properties
Harris, Joyce F. 301/975-6045	• Data acquisitions • Digitization and data entry
Kaiser, Debra L. 301/975-6759	• Ferroelectric oxide thin films • Physical properties and structures of high-temperature superconductors
Kelly, James F. 301/975-5794	• Quantitative scanning electron microscopy • Image analysis • Microstructure analysis • Powder standards
Krause, Ralph F., Jr. 301/975-5781	• Creep in flexure and tension • Fracture mechanics • Hot pressing • Chemical thermodynamics
Levine, Lyle 301/975-6032	• X-ray scattering • Defects structure in crystals
Long, Gabrielle G. 301/975-5975	• Small-angle x-ray and neutron scattering • Ceramic microstructure evolution as a function of processing • X-ray optics
Luecke, William 301/975-5744	• Creep/creep rupture • Mechanical test development
Lum, Lin-Sien H. 301/975-3674	• Powder characterization • Instrumental analysis
McGuiggan, Patricia M. 301/975-4599	• Microtribology • Surface force measurement

Minor, Dennis B. 301/975-5787	• Analytical scanning electron microscopy of ceramics and particulates • Powder test sample preparation • Powder characterization
Munro, Ronald G. 301/975-6127	• Materials properties of advanced ceramics • Data evaluation and validation • Analysis of data relations
Paul, Albert J. 301/975-6004	• Laser physics • Plasma diagnostics
Pei, Patrick T. 301/975-3681	• Spectroscopic and thermal characterization • Chemical coating • Powders characterization
Quinn, George D. 301/975-5765	• Mechanical property test standards • Standard reference materials • Creep testing
Ravel, Bruce 301/975-5759	• X-ray analysis • Ferroelectrics
Robins, Lawrence H. 301/975-5263	• Defect identification and distribution • Cathodoluminescence imaging and spectroscopy • Photoluminescence spectroscopy • Raman spectroscopy
Roosen, Andrew J. 301/975-6166	• Microstructural modeling • Computer simulation
Rotter, Lawrence D. 301/975-6603	• Measurement of electro-optic coefficients • Photorefractive effect • Optical spectroscopy of thin films
Schenck, Peter K. 301/975-5758	• Emission and laser spectroscopy • Thin-film deposition • Computer graphics and image analysis • Laboratory automation

	• Plasma monitoring and control
Smith, Douglas T. 301/975-5768	• Surface forces • Charge transfer at interfaces • Adhesion and friction
Spal, Richard D. 301/975-4028	• X-ray optics • Diffraction physics • X-ray scattering
Steiner, Bruce W. 301/975-5977	• High-resolution diffraction imaging • Defects in monolithic crystals and multilayers • Non-linear optical processes
Vanderah, Terrell A. 301/975-5785	• Solid-state chemistry • Phase equilibria of microwave dielectrics
Vaudin, Mark D. 301/975-5799	• Electron microscopy • Microscopy and diffraction studies of interfaces • Computer modeling of grain-boundary phenomena • Dielectric films
Wallace, Jay S. 301/975-5984	• Mechanical test development • Ceramic coatings • Thermal analysis
Wang, Pu Sen 301/975-6104 pu.wang@nist.gov	• Solid-state nuclear magnetic resonance • Spectroscopic characterization
White, Grady S. 301/975-5752	• Thin films • Nondestructive evaluation • Subcritical crack growth • Stress measurements • Cyclic fatigue
Woicik, Joseph C.	• UV photoemission

516/344-5236
woicik@ssrl01.slac.stanford.edu

- X-ray standing waves
- Surface and interface science

Wong-Ng, Winnie
301/975-5791

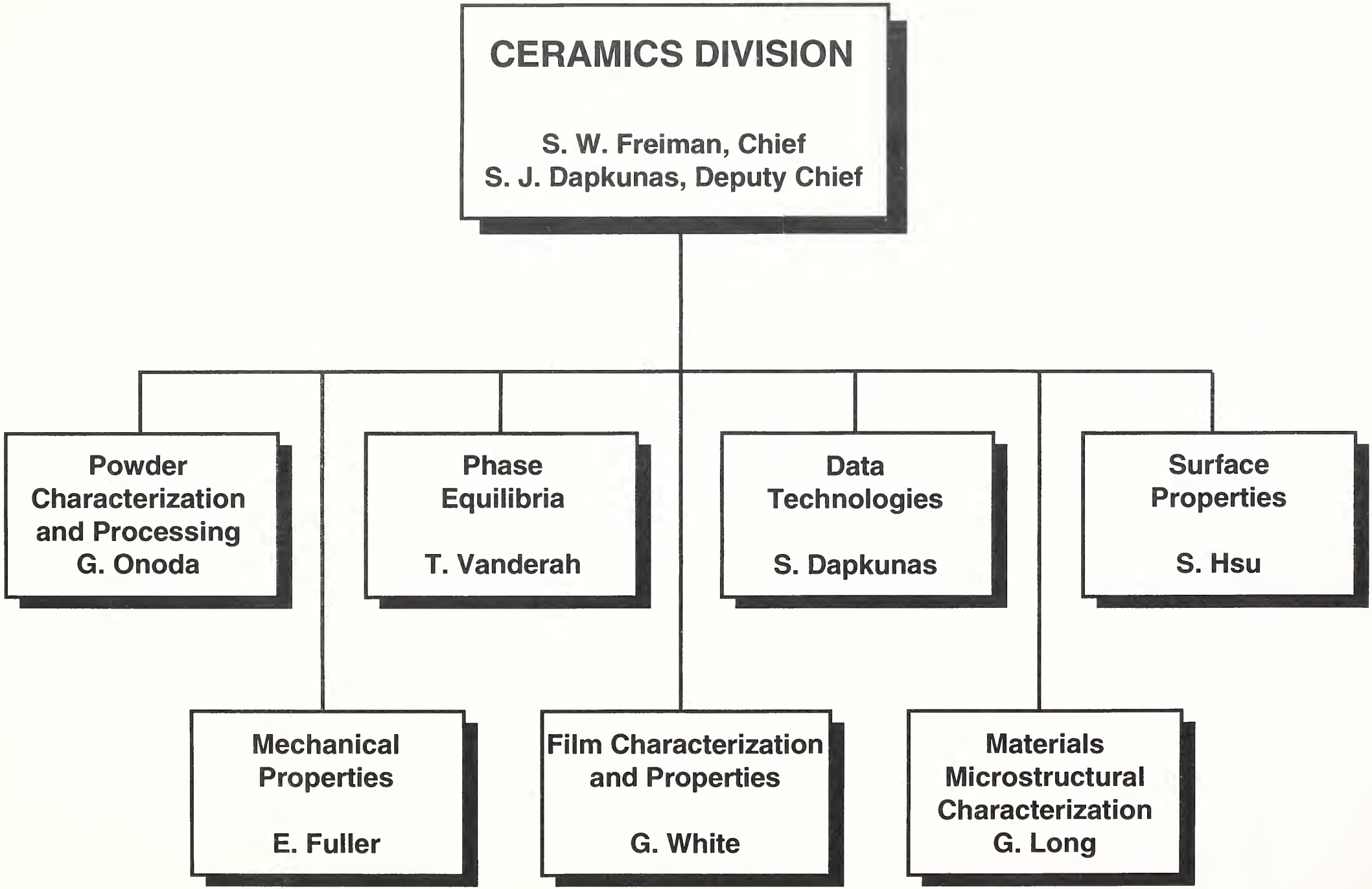
- X-ray crystallography and reference patterns
- Phase equilibria/crystal chemistry of high-T_c superconductors
- Molecular orbital calculations

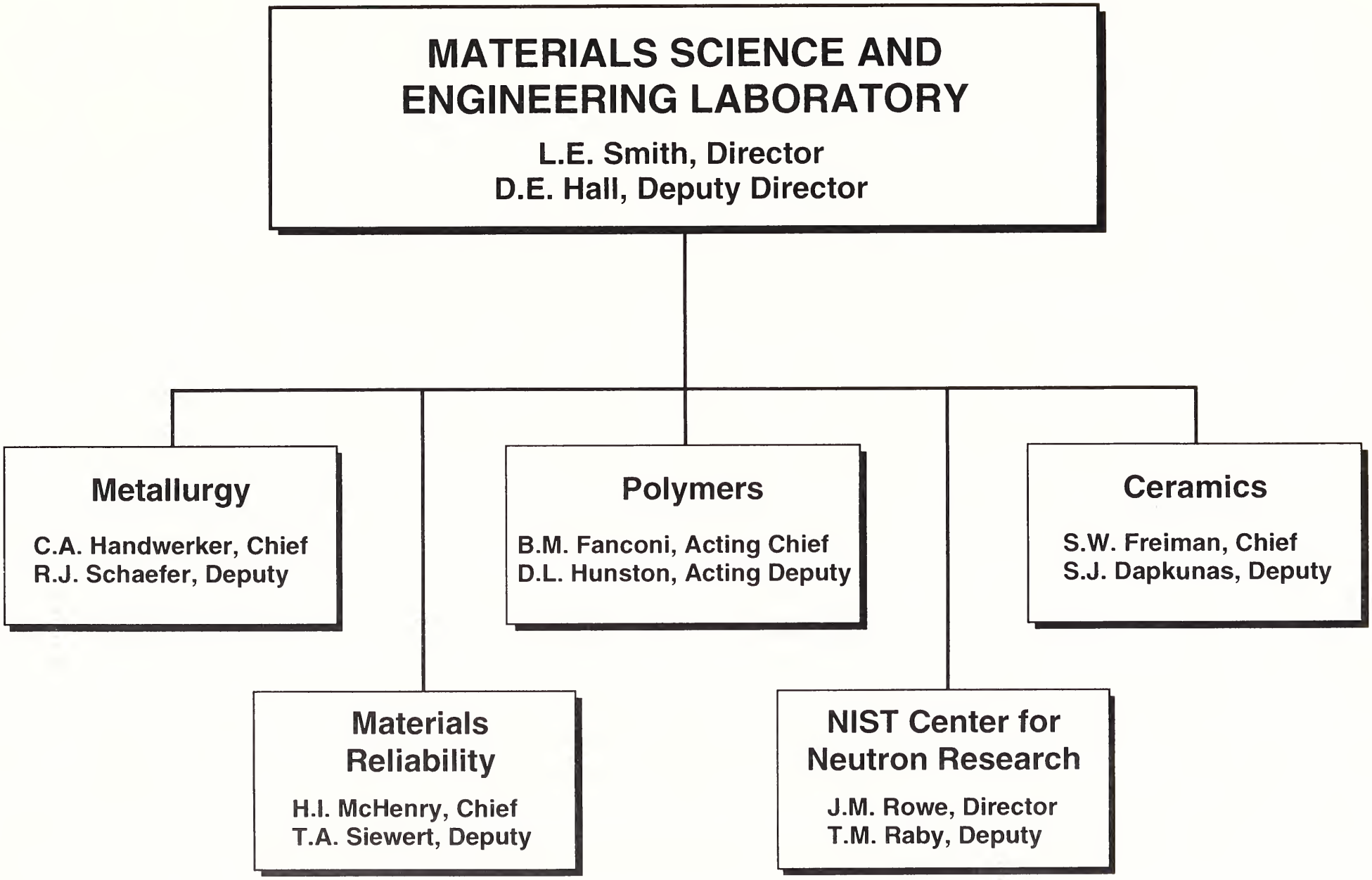
GUEST SCIENTISTS AND GRADUATE STUDENTS

Balzaretti, Naira	Institute de Fisica, Brazil
Bartlelt, Gunter	Federal Inst. of Materials Res. and Testing
Boukari, Hacene	University of Maryland
Cedeno, Christina	American Ceramic Society
Cho, Unchung	University of Illinois
Cho, Wonoh	Korea Research Inst. of Technology
Chu, Steven	State University of New York at Stony Brook
Dillingham, Jermey	University of Maryland
Fang, Hsu-Wei	University of Maryland
Farabaugh, Edward	Consultant
Febo, Ayala, Wilma	University of Puerto Rico
Fu, Zugen	State Univ. of N.Y. at Stony Brook
Haller, Wolfgang	Abbott Laboratories
Hayward, Evans	American Ceramic Society
Hryniewicz, Piotr	University of Delaware
Ilavsky, Jan	State University of New York at Stony Brook
Jemian, Peter	University of Illinois at Urbana/Champaign
Jillavenkatesa, Ajitkumar	Alfred University
Joseph, Mathew	India Gandhi Centre for Atomic Research

Kanematsu, Wataru	National Industrial Res. Inst. of Nagoya
Kieffer, John	University of Illinois
Kim, Jang-Yup	Korea University
Kim, Jung-Hun	Korean Research Institute of Standards & Sci.
Kim, Myong-Ho	Chang-Won National University
Koshy, Philip	Indian Institute of Technology
Li, Na	Beijing U. of Aeronautics & Astronautics
Lee, Yong Eui	Seoul National University
Levin, Igor	Israel Institute of Technology
Loezos, John	University of Maryland
McMurdie, Howard	Joint Center for Powder Diffraction Studies
Nagarajan, Venkatta	Indian Institute of Science
Ondik, Helen	Consultant
Piermarini, Gasper	University of Maryland
Quinn, Janet	Consultant
Ritter, Joseph	Consultant
Roberts, Ellis	Consultant
Roth, Robert	Viper Group
Ruff, Arthur	Consultant
Saigel, Anil	Consultant
Sambasivan, Sharadha	Brookhaven National Laboratory

Shen, Ming	University of Illinois
Stanimirovic, Andrej	Institute of Nuclear Sciences
Swab, Jeffrey	Army Research Laboratory
Swanson, Nils	American Ceramic Society
Turchinskaya, Marina	Consultant
Wachtman, John	Consultant
Xu, Kang	Crystal Growth and Mat. Testing Assoc.
Yeager, Glenn	Xtalonix Products Inc.
Ying, Tsi-Neng	University of Maryland
Ying, Zhanfeng	University of Illinois
Zhang, Jun	Lanzhou Institute of Chemical Physics
Zhang, Xian-Hua	University of Maryland


CERAMICS DIVISION
S. W. Freiman, Chief
S. J. Dapkunas, Deputy Chief
Powder Characterization and Processing
G. Onoda
Phase Equilibria
T. Vanderah
Data Technologies
S. Dapkunas
Surface Properties
S. Hsu
Mechanical Properties
E. Fuller
Film Characterization and Properties
G. White
Materials Microstructural Characterization
G. Long


MATERIALS SCIENCE AND ENGINEERING LABORATORY
L.E. Smith, Director
D.E. Hall, Deputy Director
Metallurgy
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R.J. Schaefer, Deputy
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Ceramics
S.W. Freiman, Chief
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Materials Reliability
H.I. McHenry, Chief
T.A. Siewert, Deputy
NIST Center for Neutron Research
J.M. Rowe, Director
T.M. Raby, Deputy

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